Polaritons and retarded interactions in nonlinear optical susceptibilities

Knoester, Jasper; Mukamel, Shaul

Published in:
The Journal of Chemical Physics

DOI:
10.1063/1.457150

Polaritons and retarded interactions in nonlinear optical susceptibilities

Jasper Knoester and Shaul Mukamel[a)]
University of Rochester, Chemistry Department, Rochester, New York 14627

(Received 27 February 1989; accepted 24 March 1989)

The role of retarded intermolecular interactions (polariton effects) in the nonlinear optical susceptibilities of condensed phases is studied. A systematic method for calculating these susceptibilities is developed, based on the derivation of reduced equations of motion which couple the electronic variables to the Maxwell (internal) electric field **E**. The susceptibilities are obtained by iteratively solving these equations in powers of **E**. Thus, the common introduction of intermediate susceptibilities with respect to either the external or the local electric field is avoided. Our method allows for the incorporation of polariton dynamics into the equations of motion. A clear distinction between microscopic and macroscopic polariton effects is made. Explicit forms for the linear ($\chi^{(1)}$) and second order ($\chi^{(2)}$) susceptibilities in molecular crystals are derived, which microscopically account for polariton–phonon scattering. Our theory provides an explanation for a recent series of linear and nonlinear optical experiments in naphtalene crystals which were found to contradict existing theories of nonlinear susceptibilities.

I. INTRODUCTION

The microscopic calculation of the linear and nonlinear optical response of molecular condensed phase systems is essential in order to relate experimental measurements to the underlying molecular dynamics. Convenient quantities which express the optical response of a medium are its linear and nonlinear susceptibilities, which are the expansion coefficients of the material polarization in terms of the Maxwell electric field.[1–3] The great merit of susceptibilities as link between theory and experiment, is that, once they are calculated, any optical process may be analyzed by using them in Maxwell's equations in conjunction with the proper boundary conditions. Traditionally, the susceptibilities are viewed as purely material quantities, which can be calculated from the isolated material Hamiltonian, and do not explicitly involve the transverse radiation field. In condensed phase systems, however, appreciable intermolecular interactions and a large density of oscillator strength give rise to retardation of polariton effects, which imply that the susceptibilities do have an explicit signature of the transverse radiation field. Recent second-harmonic generation and two-photon excited fluorescence experiments in naphthalene crystals[4] and transient grating experiments in anthracene crystals[5] clearly demonstrate such effects, and point out the necessity to formulate the microscopic theory of optical response in a way that systematically accounts for retardation. Addressing this problem is the main goal of this paper.

If retardation effects are neglected, linear and nonlinear response theory may be used to express the susceptibilities as correlation functions of material quantities calculated *in total absence of the transverse radiation field*.[6] They may thus be expressed in terms of properties (e.g., the energy, the transition dipole, etc.) of the eigenstates of the material Hamiltonian containing the *instantaneous* Coulomb interactions only. In most practical cases, the calculation of the eigenstates poses too big a problem, so that one has to use approximate methods, such as the local field approach, in which the susceptibilities are given by the single molecule hyperpolarizabilities multiplied by local field correction factors.[3,7] An important and illustrative case for which the material Hamiltonian can be diagonalized, is the infinite crystal. Its eigenstates are the excitons,[8,9] which in linear approximation may be viewed as bosons (harmonic oscillators) and yield the following, often quoted, form for the (linear) dielectric function[10,11]:

$$\varepsilon(\mathbf{k},\omega) = \mathbf{1} + \sum_j \frac{4\pi\alpha_j(\mathbf{k})\omega_j^2(\mathbf{k})}{\omega_j^2(\mathbf{k}) - \omega^2 - i\omega\Gamma_j(\mathbf{k})}, \tag{1.1}$$

where $\omega_j(\mathbf{k})$ is the dispersion of exciton branch j, $\alpha_j(\mathbf{k})$ is a measure of the oscillator strength of transition j and $\Gamma_j(\mathbf{k})$ is a phenomenologically added damping constant, which is thought of as being inversely proportional to the lifetime of exciton j. We note that this response function has the same form as the molecular polarizability in the Lorentz model, except that the resonances occur at the exciton frequencies at wave vector $\mathbf{k}$ instead of at the bare molecular eigenfrequencies. In a similar way, higher order susceptibilities will have resonances at the exciton frequencies. The damping constants occurring in the susceptibilities of condensed phases are quantities of paramount importance, because they directly reflect the microscopic dynamics. For example, in a pure crystal, $\Gamma_j(\mathbf{k})$ is usually due to scattering of excitons on phonons.

As is well known, even if the susceptibilities themselves are considered purely material quantities [such as Eq. (1.1)], the optical signal will still contain effects of retarded interactions, which are introduced when consistently solving Maxwell's equations with the aid of the susceptibilities. This results in phase matching and also gives rise to the fact that the polarization field of certain order does not only involve the susceptibility of that order but also those of lower orders (cascading).[2,12] Such effects are *macroscopic* retardation or polariton effects, as they arise purely from the solution of the macroscopic Maxwell equations, irrespective of

[a)] Camile and Henry Dreyfus Teacher/Scholar.

 0021-9606/89/140989-19$02.10

the microscopic form of the susceptibilities. Formally, however, it is clear that the susceptibilities, too, must depend on the retarded interactions mediated by the transverse radiation field. The reason is that quantum mechanically the radiation field cannot be switched off, so that the material system with Coulomb interactions can never be considered a really isolated system. The interaction of the charges in the medium with the transverse radiation modes is responsible for radiative decay and Lamb shifts.[13] These retardation effects can easily be taken into account in the optical susceptibilities by using phenomenological arguments; a rigorous treatment has been given in Ref. 14. There is, however, a more profound way in which retarded interactions enter the picture. In the case of a sufficiently pure crystal at low temperature, the eigenmodes of the material Hamiltonian (the excitons) couple strongly to those of the transverse radiation field (the photons) to form new normal modes: the polaritons.[15–20] The presence of phonons in the crystal should then be considered as a perturbation to the polariton propagation. Even though polaritons couple to phonons through their exciton components, the "particles" to be scattered on the phonons are the polaritons. Since the forms of the dispersion curves and the group velocities of polaritons and excitons differ widely, their scattering rates must also be expected to be very distinct. Therefore, exciton damping rates may be entirely irrelevant to the broadening of optical lineshapes. Instead, polariton damping rates may enter the susceptibilities, as is clearly suggested by the experiments of Small and co-workers in naphthalene crystals.[4] We will call such effects *microscopic* retardation or polariton effects, because they are characterized by an explicit signature of the transverse radiation field in the microscopic form of the susceptibilities. The present paper focuses on a systematic inclusion of these effects.

Microscopic studies of polariton dephasing rates due to scattering with other polaritons, phonons, etc., have been conducted before, and several authors have argued that $\Gamma_j(\mathbf{k})$ in Eq. (1.1) is in fact determined by these rates.[21–24] So far, however, a systematic theory showing how in general polariton scattering processes affect the susceptibilities is lacking. Agranovich and Konobeev, using Green function techniques, were the first to incorporate scattering of polaritons into the *linear* dielectric response.[25] The extension of these ideas to nonlinear optical susceptibilities is a complex issue. To our knowledge, the only general scheme for a microscopic formulation of nonlinear optics in terms of polaritons is due to Ovander.[18] His motivation was not the proper treatment of damping, but, rather, his discontent with the concept of susceptibilities, which he abandons. One of his arguments is that susceptibilities have (when damping is neglected) poles at the exciton frequencies, which are not the eigenfrequencies of the full (material and radiation) system. His method, on which we will elaborate in Sec. VII, directly yields absorption and emission rates of polaritons. In other words, the calculation of the optical signal is not separated into the two steps of first calculating the susceptibilities and then solving the Maxwell equations. This separation has been proven extremely useful in nonlinear optics, because it postpones the introduction of geometrical and boundary effects to a later stage of the calculation. We have to bear in mind, however, that, when working with susceptibilities, retarded interactions enter the optical signal in both the microscopic and the macroscopic step of its evaluation. In this paper, we show how this can be achieved without overcounting interactions.

The outline of this paper is as follows. In Sec. II, we present the microscopic model (a lattice of multilevel molecules) and the Hamiltonian. Our microscopic starting point does not differ in any important respect from the one common in the exciton–polariton literature, but we describe it in reasonable detail to keep the paper self-contained and to set the notation. The difference with previous theories lies in the approach to calculate the optical response from this model. Our method is based on the derivation of reduced equations of motion for the electronic (excitonic) and the radiation operators (Sec. III). From the linear part of these coupled equations, the polaritons are obtained in Sec. IV. In Sec. V, we introduce phonons in the system, and, using a projection technique, we extend the reduced equations of motion to contain the effects of polariton dephasing by phonons. Solving the resulting equations for the excitonic variables iteratively in terms of the macroscopic electric field modes, yields the nonlinear susceptibilities with the microscopic retardation effects properly included. In Sec. VI, we give explicit expressions for the linear and second order susceptibilities, and discuss their general forms. A more detailed analysis, carried out in the light of the aforementioned experiments by the Small group, follows in Sec. VII, along with a critical discussion of Ovander's theory. The Appendices A and B contain technical details on the evaluation of the projection kernel used in Sec. V and on the iterative calculation of the susceptibilities.

II. MICROSCOPIC MODEL AND HAMILTONIAN

We consider a lattice with N sites occupied by identical multilevel molecules. The eigenstates of the isolated molecules are assumed known, and denoted by $|mf\rangle$, where m labels the molecule and f the level. The set of molecular eigenstates is chosen real and orthonormal and the overlap between the wave functions of different molecules in the crystal is neglected, which is a good approximation for many molecular crystals. We thus have $\langle mf|ng\rangle = \delta_{m,n}\delta_{f,g}$. The energy of level f is $\hbar\Omega_f$, which for the ground level ($f=0$) is chosen zero, and the dipole matrix elements are denoted

$$\boldsymbol{\mu}_{fg} = \langle mf|\hat{\boldsymbol{\mu}}_m|mg\rangle, \tag{2.1}$$

where $\hat{\boldsymbol{\mu}}_m$ is the dipole operator of molecule m. Throughout this paper, an operator is indicated by a caret, e.g., $\hat{O}$; its expectation value at time t is denoted $\langle\hat{O}(t)\rangle$. Since the wave functions have been chosen real, we have $\boldsymbol{\mu}_{fg} = \boldsymbol{\mu}_{gf}$, and furthermore we will assume that the molecules are nonpolar, so that $\boldsymbol{\mu}_{ff} = 0$. The energies and dipole matrix elements do not depend on m, as all molecules are identical. We confine ourselves to a lattice with one molecule per unit cell to avoid the important physics from getting lost in a cumbersome notation. We note, however, that extension of the results presented here to more complicated crystal structures is formally readily obtained, and the equations of motion to be derived

in Sec. III, can even be obtained for arbitrary molecular configurations.

The operator notation which we will use is straightforward, but slightly different from the one introduced by Agranovich into the theory of excitons.[8,9,17] It is, however, based on exactly the same concept of second quantization. We define the transition operator $\hat{B}_{mfg}$ by its action on the total crystal state. If molecule m is in level g, $\hat{B}_{mfg}$ takes it to level f, without affecting the other molecules; otherwise, $\hat{B}_{mfg}$ yields zero. We note that the usual Pauli creation and annihilation operators $\hat{B}^{\dagger}_{mf}$ and $\hat{B}_{mf}$ of an excitation on the fth excited level of molecule m are in our notation given by $\hat{B}_{mf0}$ and $\hat{B}_{m0f}$, respectively.[9,17] The commutation relations of the transition operators clearly read

$$[\hat{B}_{mfg},\hat{B}_{nf'g'}] = (\hat{B}_{mfg'}\delta_{gf'} - \hat{B}_{mf'g}\delta_{fg'})\delta_{mn}. \tag{2.2}$$

Of course, all electronic operators may be expressed in terms of these operators, and in particular the polarization field (which plays a crucial role in the description of optical processes) can be written as

$$\hat{\mathbf{P}}(\mathbf{r}) = \sum_m \hat{\boldsymbol{\mu}}_m \delta(\mathbf{r}-\mathbf{r}_m) = \sum_m \sum_{f,g} \boldsymbol{\mu}_{fg}\hat{B}_{mfg}\delta(\mathbf{r}-\mathbf{r}_m), \tag{2.3}$$

where $\mathbf{r}_m$ denotes the position of molecule m.

The Hamiltonian of the crystal, without contributions from the transverse radiation field, is written in its general form as:

$$\hat{H}_{\rm exc} = \sum_m \sum_f \hbar\Omega_f \hat{B}_{mff} + \frac{1}{2}\sum_{m,n}{}' \sum_{f,g,f',g'} \hbar V_{mn}(gg';ff')\hat{B}_{mgf}\hat{B}_{ng'f'}. \tag{2.4}$$

We remark that this is only the electronic (or excitonic) part of the material Hamiltonian, i.e., the molecules are assumed to have fixed positions at the lattice sites. Phonon contributions will be considered in Sec. V. The first term in Eq. (2.4) is the total electronic energy of the individual molecules, whereas the second term accounts for instantaneous (Coulomb) interactions (the prime on the summation excludes terms with $m=n$). The interaction matrix elements are defined in the usual way:

$$\hbar V_{mn}(gg';ff') = \langle mg,ng'|\hbar\hat{V}_{mn}|mf,nf'\rangle, \tag{2.5}$$

with $\hbar\hat{V}_{mn}$ the interaction operator between the molecules m and n. Since the interaction is symmetric in m and n, we have $V_{mn}(gg';ff') = V_{mn}(g'g;f'f)$. Furthermore, as the wave functions have been chosen real and exchange is neglected, the matrix elements are real and invariant under interchange of f and g and (or) f' and g'. We will assume dipole–dipole interactions, so that

$$\hbar V_{mn}(gg';ff') = \frac{\boldsymbol{\mu}_{gf}\cdot\boldsymbol{\mu}_{g'f'}}{r_{mn}^3} - \frac{(\boldsymbol{\mu}_{gf}\cdot\mathbf{r}_{mn})(\boldsymbol{\mu}_{g'f'}\cdot\mathbf{r}_{mn})}{r_{mn}^5}, \tag{2.6}$$

where $\mathbf{r}_{mn}$ is the position of molecule m relative to that of molecule n. This coupling vanishes for $f=g$ or $f'=g'$ in the case of nonpolar molecules.

We work in the Coulomb gauge for the radiation field: div $\mathbf{A}=0$, where $\mathbf{A}$ is the vector potential, and we use the minimal coupling Hamiltonian in the electric dipole approximation. Previously, a theory of nonlinear optics was presented in which the multipolar Hamiltonian proved to be extremely useful.[14] In the present paper, however, we want to focus on exciton and polariton properties, and these elementary excitations are treated in an easier way in the minimal coupling Hamiltonian, which incorporates explicitly intermolecular interactions. The interaction Hamiltonian of the transverse radiation field with the crystal is thus:

$$\hat{H}_{\rm int} = -\frac{e}{Mc}\sum_m \hat{\mathbf{p}}_m\cdot\hat{\mathbf{A}}(\mathbf{r}_m) + \frac{Ze^2}{2Mc^2}\sum_m [\hat{\mathbf{A}}(\mathbf{r}_m)]^2. \tag{2.7}$$

Here $M(e)$ stands for the electron mass (charge), c denotes the vacuum velocity of light, and $\hat{\mathbf{p}}_m$ is the total canonical momentum of the Z optically active electrons of molecule m. Using the commutation relation[8]

$$\hat{\mathbf{p}}_m = \frac{iM}{\hbar e}[\hat{H}_m,\hat{\boldsymbol{\mu}}_m], \tag{2.8}$$

with $\hat{H}_m$ the isolated molecular Hamiltonian, an expression for $\hat{\mathbf{p}}_m$ in second quantized form is obtained:

$$\hat{\mathbf{p}}_m = \frac{iM}{e}\sum_{f,g}\Omega_{fg}\boldsymbol{\mu}_{fg}\hat{B}_{mfg}, \tag{2.9}$$

where $\Omega_{fg}\equiv\Omega_f-\Omega_g$. It is useful for future reference to give the oscillator sum rule, which follows from the commutator of the electronic position and momentum[8]:

$$\sum_f \Omega_f\boldsymbol{\mu}_{0f}\boldsymbol{\mu}_{0f} = \frac{\hbar e^2}{2M}Z\,\mathbf{1}, \tag{2.10}$$

where dyad notation is used and $\mathbf{1}$ is the three dimensional unit matrix. The radiation field, too, is treated in second quantization:

$$\hat{\mathbf{A}}(\mathbf{r}) = \sum_{\mathbf{k},\lambda}\left(\frac{2\pi\hbar c^2}{V\omega_k}\right)^{1/2}(\hat{a}_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}} + \hat{a}^{\dagger}_{\mathbf{k}\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}})\mathbf{e}_{\mathbf{k}\lambda}, \tag{2.11}$$

where V is the quantization volume, which is taken equal to the volume of the crystal (and will be sent to infinity eventually) and $\omega_k\equiv kc$. As usual, $\hat{a}^{\dagger}_{\mathbf{k}\lambda}$ ($\hat{a}_{\mathbf{k}\lambda}$) denotes the creation (annihilation) operator of a photon with wave vector $\mathbf{k}$ and polarization λ, subject to the Bose commutation relations

$$[\hat{a}_{\mathbf{k}\lambda},\hat{a}^{\dagger}_{\mathbf{k}'\lambda'}] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{\lambda\lambda'}, \quad [\hat{a}_{\mathbf{k}\lambda},\hat{a}_{\mathbf{k}'\lambda'}] = 0. \tag{2.12}$$

Finally, $\mathbf{e}_{\mathbf{k}\lambda}$ is the unit polarization vector of mode $\mathbf{k}\lambda$, which is taken real and such that $\mathbf{e}_{-\mathbf{k}\lambda} = \mathbf{e}_{\mathbf{k}\lambda}$. The transverse electric field, $\mathbf{E} = -c^{-1}\partial\mathbf{A}/\partial t$, is in the minimal coupling Hamiltonian the conjugate momentum to the vector potential, and is given by

$$\hat{\mathbf{E}}(\mathbf{r}) = i\sum_{\mathbf{k},\lambda}\left(\frac{2\pi\hbar\omega_k}{V}\right)^{1/2}(\hat{a}_{\mathbf{k}\lambda}e^{i\mathbf{k}\cdot\mathbf{r}} - \hat{a}^{\dagger}_{\mathbf{k}\lambda}e^{-i\mathbf{k}\cdot\mathbf{r}})\mathbf{e}_{\mathbf{k}\lambda}. \tag{2.13}$$

We will not consider response to longitudinal electric fields in this paper. The Hamiltonian of the unperturbed radiation field has the familiar form

$$\hat{H}_{\rm rad} = \sum_{\mathbf{k},\lambda}\hbar\omega_k\hat{a}^{\dagger}_{\mathbf{k}\lambda}\hat{a}_{\mathbf{k}\lambda}. \tag{2.14}$$

The total Hamiltonian of the crystal electronic degrees of freedom and the radiation field is now given by the sum of Eqs. (2.4), (2.7), and (2.14)

$$\hat{H}_0 = \hat{H}_{\rm exc} + \hat{H}_{\rm rad} + \hat{H}_{\rm int}. \tag{2.15}$$

Finally, we will use the following spatial and temporal Fourier transforms in this paper:

$$f(\mathbf{k}) = \int_V f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}, \tag{2.16a}$$

$$f(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{k}} f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{2.16b}$$

$$g(\omega) = \int_{-\infty}^{+\infty} g(t) e^{i\omega t}\, dt, \tag{2.16c}$$

$$g(t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} g(\omega) e^{-i\omega t}\, d\omega. \tag{2.16d}$$

III. REDUCED EQUATIONS OF MOTION

In this section, we derive reduced equations of motion for the electronic and radiation field variables in the absence of phonons. Clearly, coupled equations of motion for the expectation values of the transition operators $\hat{B}_{mfg}$ and the photon creation and annihilation operators, enable one to calculate the coupled dynamics of the polarization field and the electric field, and, more specifically, to evaluate susceptibilities. We start by deriving the Heisenberg equations of motion for the operators of interest. At this point, it is common to assume that the Pauli creation and annihilation operators obey Bose commutation relations $[\hat{B}_{mf}, \hat{B}^{\dagger}_{mg}] = \delta_{fg}$.[8,9,16–19] This, however, is a linear approximation, which is not consistent with the aim to describe nonlinear optics. (see Sec. VII). It is essential, therefore, to use the exact commutators given by Eq. (2.2). Of course, molecular operators commute with radiation operators. The Heisenberg equations of motion then read (the time dependence of the operators is implicit)

$$\begin{aligned}\frac{d}{dt}\hat{a}_{\mathbf{k}\lambda} = &-i\omega_{\mathbf{k}}\hat{a}_{\mathbf{k}\lambda} - \frac{4\pi\rho i}{\hbar\omega_{\mathbf{k}}}\sum_f \Omega_f \sum_{\lambda'}(\boldsymbol{\mu}_{0f}\cdot\mathbf{e}_{\mathbf{k}\lambda})\\ &\times(\boldsymbol{\mu}_{0f}\cdot\mathbf{e}_{\mathbf{k}\lambda'})(\hat{a}_{\mathbf{k}\lambda'} + \hat{a}^{\dagger}_{-\mathbf{k}\lambda'})\\ &+\frac{ie}{M}\left(\frac{2\pi}{\hbar\omega_k V}\right)^{1/2}\sum_m(\hat{\mathbf{p}}_m\cdot\mathbf{e}_{\mathbf{k}\lambda})e^{-i\mathbf{k}\cdot\mathbf{r}_m},\end{aligned} \tag{3.1}$$

and

$$\begin{aligned}\frac{d}{dt}\hat{B}_{mfg} = &\,i\Omega_{fg}\hat{B}_{mfg} + i\sum_{n\neq m}\sum_{f',g'}\hat{B}_{nf'g'}\sum_h[V_{mn}(hf';fg')\hat{B}_{mhg}\\ &- V_{mn}(gf';hg')\hat{B}_{mfh}]\\ &+\frac{1}{\hbar c}\hat{\mathbf{A}}(\mathbf{r}_m)\cdot\sum_h[\boldsymbol{\mu}_{hf}\Omega_{hf}\hat{B}_{mhg} - \boldsymbol{\mu}_{gh}\Omega_{gh}\hat{B}_{mfh}].\end{aligned} \tag{3.2}$$

Here $\rho \equiv N/V$ denotes the average density of molecules. In the derivation of Eq. (3.1), the role of Umklapp processes has neglected. Furthermore, the oscillator sum rule has been used by writing the $\hat{\mathbf{A}}^2$ term in $\hat{H}_{\rm int}$ as $\hat{\mathbf{A}}\cdot\mathbf{1}\cdot\hat{\mathbf{A}}$ and inferring Eq. (2.10). The reason for this will become clear in Sec. IV. We remark that Eq. (3.1) and its Hermitian conjugate for $a^{\dagger}_{\mathbf{k}\lambda}$ are consistent with the Maxwell equations for the vector potential and the transverse electric field.

In an infinite crystal, it is natural to choose a $\mathbf{k}$-space representation. We define

$$\hat{B}_{\mathbf{k}fg} = \frac{1}{\sqrt{N}}\sum_m \hat{B}_{mfg} e^{-i\mathbf{k}\cdot\mathbf{r}_m}, \tag{3.3a}$$

and conversely

$$\hat{B}_{mfg} = \frac{1}{\sqrt{N}}\sum_{\mathbf{k}\,1\mathrm{BZ}} \hat{B}_{\mathbf{k}fg} e^{i\mathbf{k}\cdot\mathbf{r}_m}, \tag{3.3b}$$

where the $\mathbf{k}$ summation extends over the first Brillouin zone (1BZ) of the reciprocal lattice only. Equation (3.2) is now transformed to

$$\begin{aligned}\frac{d}{dt}\hat{B}_{\mathbf{k}fg} = &\,i\Omega_{fg}\hat{B}_{\mathbf{k}fg} + \frac{i}{\sqrt{N}}\sum_{\mathbf{k}'\,1\mathrm{BZ}}\sum_{f',g'}\hat{B}_{\mathbf{k}'f'g'}\sum_h\\ &\times[V_{\mathbf{k}'}(hf';fg')\hat{B}_{\mathbf{k}-\mathbf{k}',hg} - V_{\mathbf{k}'}(gf';hg')\hat{B}_{\mathbf{k}-\mathbf{k}',fh}]\\ &+\frac{1}{\hbar c}\frac{1}{V}\sum_{\mathbf{k}'}\hat{\mathbf{A}}(\mathbf{k}')\cdot\sum_h[\boldsymbol{\mu}_{hf}\Omega_{hf}\hat{B}_{\mathbf{k}-\mathbf{k}',hg}\\ &-\boldsymbol{\mu}_{gh}\Omega_{gh}\hat{B}_{\mathbf{k}-\mathbf{k}',fh}],\end{aligned} \tag{3.4}$$

where

$$V_{\mathbf{k}}(f_1f_2;f_3f_4) \equiv \sum_{m\neq n} V_{mn}(f_1f_2;f_3f_4)e^{-i\mathbf{k}\cdot\mathbf{r}_m} \tag{3.5}$$

and $\hat{\mathbf{A}}(\mathbf{k})$ is the continuous space Fourier transform [cf. Eq. (2.16)] of $\hat{\mathbf{A}}(\mathbf{r})$. We are ultimately interested in the expectation values of the polarization field and the electric field. Equations (3.1) and (3.4), however, do not yield a closed and exact set of equations for expectation values in a straightforward way (namely, by just taking the expectation values of the equations), because the right hand side of Eq. (3.4) contains operator products. The formal solution of this problem requires either an infinite hierarchy of equations, in which every new product of operators generated by the Heisenberg equations of motions is added as a new variable,[26] or the derivation of closed and exact equations of motion for a selected set of relevant variables by a projection operator technique.[27] Both approaches are cumbersome in practice, and here we will simply adopt a factorization approximation: the expectation value of a product of radiation and material operators or of two operators acting on different molecules will be factored into the product of the separate expectation values. This is equivalent to truncating the hierarchy after the first step and also to the lowest order (in the intermolecular interaction and the molecule–radiation interaction) result of a projection operator technique. A systematic way of improving upon this approximation is, e.g., obtained by using the projection method presented in Ref. 14. In the present approximation, we obtain for the electronic variables:

$$\frac{d}{dt}\langle\hat{B}_{\mathbf{k}fg}(t)\rangle = i\Omega_{fg}\langle\hat{B}_{\mathbf{k}fg}(t)\rangle + \frac{i}{\sqrt{N}}\sum_{\mathbf{k}'}^{1\mathrm{BZ}}\sum_{f',g'}\langle\hat{B}_{\mathbf{k}'f'g'}(t)\rangle\sum_{h}[V_{\mathbf{k}'}(hf';fg')\langle\hat{B}_{\mathbf{k}-\mathbf{k}',hg}(t)\rangle - V_{\mathbf{k}'}(gf';hg')\langle\hat{B}_{\mathbf{k}-\mathbf{k}',fh}(t)\rangle]$$

$$+\frac{1}{\hbar c}\frac{1}{V}\sum_{\mathbf{k}'}\langle\hat{\mathbf{A}}(\mathbf{k}',t)\rangle\cdot\sum_{h}[\boldsymbol{\mu}_{hf}\Omega_{hf}\langle\hat{B}_{\mathbf{k}-\mathbf{k}',hg}(t)\rangle - \boldsymbol{\mu}_{gh}\Omega_{gh}\langle\hat{B}_{\mathbf{k}-\mathbf{k}',fh}(t)\rangle]. \tag{3.6}$$

It is important and instructive at this point to note that in the absence of additional degrees of freedom other than electronic and radiation modes, Eq. (3.6) suffices to calculate susceptibilities. To this end, one transforms the equation to the frequency domain and uses the relation $\mathbf{A}(\mathbf{k},\omega) = -ic\mathbf{E}(\mathbf{k},\omega)/\omega$ to obtain material equations which contain the Fourier components of the electric field. The nth order susceptibility, characterizing the material response to a small number of plane waves given by their amplitudes $\mathbf{E}(\mathbf{k}_1,\omega_1),\ldots,\mathbf{E}(\mathbf{k}_n,\omega_n)$, is then obtained by iteratively solving the material variables $\langle\hat{B}_{\mathbf{k}fg}(\omega)\rangle$ in terms of these amplitudes, which directly yields the expansion of the polarization field [cf. Eq. (2.3)] in terms of the electric field. Thus, the equations for the radiation fields (Maxwell's equations) are irrelevant to the evaluation of the susceptibilities, which may therefore be viewed as purely material quantities. Now suppose, however, that other degrees of freedom couple to the electronic and radiation variables. For concreteness, we consider the example of a phonon bath, on which we focus in this paper. Phonons couple to the excitonic variables (see Sec. V). Therefore, if excitons are considered the eigenmodes in the crystal, the effect of phonons can be incorporated by a dephasing of the excitons caused by their scattering on phonons. This introduces imaginary parts in the frequencies Ω_{fg} in Eq. (3.6) and broadening of the optical lineshapes. Since at low temperature, however, the eigenstates of the crystal are strongly mixed collective exciton–photon modes (polaritons),[16–20] the actual effect of phonons is a perturbation of the polariton propagation. For a correct incorporation of phonon damping in the susceptibilities, it is thus necessary to consider the dynamics of the polaritons explicitly, and this requires the use of the equations of motion for the radiation field [Eq. (3.1)] in addition to Eq. (3.6).

IV. THE POLARITON TRANSFORMATION

In this section, we derive the form of the polaritons in terms of exciton and photon creation and annihilation operators. The polaritons are the self-consistent solutions to the set of Eqs. (3.1) and (3.4). Clearly such solutions cannot be obtained in practice, since the equations are nonlinear. Rather, the polaritons are the eigenmode solutions to a linearized set of equations, which is obtained by setting $\hat{B}_{mff} = \hat{1}\delta_{f0}$ or, equivalently, $\hat{B}_{kff} = \sqrt{N}\Sigma_{\mathbf{G}}\delta_{\mathbf{k},2\pi\mathbf{G}}\delta_{f0}$ ($\mathbf{G}$ runs over the reciprocal lattice), and by only keeping terms which are linear in $\hat{B}_{\mathbf{k}0f}\equiv\hat{B}_{\mathbf{k}f},\hat{B}_{\mathbf{k}f0}\equiv\hat{B}^{\dagger}_{-\mathbf{k}f}(f\neq 0)$ and $\hat{\mathbf{A}}$. The rationale for this linearization is that at low temperature all molecules are in the ground state in the absence of a radiation field ($\hat{B}_{mff} = \hat{1}\delta_{f0}$), and that it takes two interactions with the radiation field to change the ground state population to either an excited state population or to a coherence between two excited states. Furthermore, the coherences between the ground state and an excited level can be created by one interaction with the radiation field, so that these are linear. Performing the linearization, one arrives at

$$\frac{d}{dt}\hat{a}_{\mathbf{k}\lambda} = -i\omega_{\mathbf{k}}\hat{a}_{\mathbf{k}\lambda} - \frac{4\pi\rho i}{\hbar\omega_{\mathbf{k}}}\sum_{f}\Omega_f \times\sum_{\lambda'}(\boldsymbol{\mu}_{0f}\cdot\mathbf{e}_{\mathbf{k}\lambda})(\boldsymbol{\mu}_{0f}\cdot\mathbf{e}_{\mathbf{k}\lambda'})(\hat{a}_{\mathbf{k}\lambda'} + \hat{a}^{\dagger}_{-\mathbf{k}\lambda'}) + \sum_{f}\left(\frac{2\pi\rho}{\hbar\omega_{\mathbf{k}}}\right)^{1/2}\Omega_f(\boldsymbol{\mu}_{0f}\cdot\mathbf{e}_{\mathbf{k}\lambda})(\hat{B}_{\mathbf{k}f} - \hat{B}^{\dagger}_{-\mathbf{k}f}), \tag{4.1a}$$

and

$$\frac{d}{dt}\hat{B}_{\mathbf{k}f} = -i\Omega_f\hat{B}_{\mathbf{k}f} - i\sum_{f'}V_{\mathbf{k}}(0f';f0)(\hat{B}_{\mathbf{k}f'} + \hat{B}^{\dagger}_{-\mathbf{k}f'}) - \sum_{\lambda}\left(\frac{2\pi\rho}{\hbar\omega_{\mathbf{k}}}\right)^{1/2}\Omega_f(\boldsymbol{\mu}_{0f}\cdot\mathbf{e}_{\mathbf{k}\lambda})(\hat{a}_{\mathbf{k}\lambda} + \hat{a}^{\dagger}_{-\mathbf{k}\lambda}). \tag{4.1b}$$

The polaritons at wave vector $\mathbf{k}$ are elementary modes with annihilation operators $\hat{\xi}_{\mathbf{k}l}$ which are linear combinations of the operators $\hat{a}_{\mathbf{k}\lambda},\hat{a}^{\dagger}_{-\mathbf{k}\lambda},\hat{B}_{\mathbf{k}f}$ and $\hat{B}^{\dagger}_{-\mathbf{k}f}$ (all λ,f) such that $d\hat{\xi}_{\mathbf{k}l}/dt = -i\omega_{\mathbf{k}l}\hat{\xi}_{\mathbf{k}l}$, where the linearized equations of motion Eqs. (4.1) are used to evaluate $d\hat{\xi}_{\mathbf{k}l}/dt$. The subscript l labels the polariton branch. Equivalently, assuming Bose commutators for $\hat{B}_{\mathbf{k}f}$ and $\hat{B}^{\dagger}_{\mathbf{k}f}$, the polaritons diagonalize that part $H_0^{(2)}$ of the Hamiltonian Eq. (2.15) which is quadratic in the $\hat{a}_{\mathbf{k}\lambda},\hat{a}^{\dagger}_{-\mathbf{k}\lambda},\hat{B}_{\mathbf{k}f}$ and $\hat{B}^{\dagger}_{-\mathbf{k}f}$[16–20,28]:

$$H_0^{(2)} = \sum_{\mathbf{k}l}\omega_{\mathbf{k}l}\hat{\xi}^{\dagger}_{\mathbf{k}l}\hat{\xi}_{\mathbf{k}l}, \tag{4.2a}$$

subject to the condition

$$[\hat{\xi}_{\mathbf{k}l},\hat{\xi}^{\dagger}_{\mathbf{k}'l'}] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{ll'}. \tag{4.2b}$$

If K represents the number of molecular excited states, the solution of the polaritons in general involves a $(K+2)$-dimensional eigenvalue problem, to $K+2$ distinct polariton branches. For simplicity, we will decouple the equations of motion for the different excited levels f, so that we only have to consider one excited molecular state explicity, treating the other levels as the source of a background index of refraction, which slowly varies with frequency and wave vector.[8,19] The role of "mixing" of different molecular levels f and g has been investigated in the diagonalization of $\hat{H}_{\mathrm{exc}}$ [Eq. 2.4],[8] which yields the excitons and is often considered as intermediate step in the transformation from the molecular operators to the polaritons. It can be shown that this mixing is only important as long as $\Omega_{fg}^2 < |V_{\mathbf{k}}(0f;g0)|^2$, which for molecular crystals generally implies a very small separation of levels f and g. With this result in mind, we perform a level-by-level calculation of polaritons, where it should be understood that the polariton operators and dispersion curves obtained by

considering a certain level f have only meaning at frequencies close to Ω_f. To obtain the total dispersion diagram of the polaritons in this treatment, one connects the upper and lower polariton curves belonging to subsequent levels in the frequency region intermediate between the two levels, where both curves approach the photon dispersion curve with a background index of refraction (Fig. 1). In practice, this approximation means that (i) only one term is retained in the sum over levels occuring in Eqs. (4.1); (ii) the velocity of light is replaced by $c \to c/\eta$ and the photon dispersion $\omega_{\mathbf{k}} \to \bar{\omega}_{\mathbf{k}} \equiv kc/\eta$, where η is the background index of refraction whose tensor nature will be neglected here; and (iii) the matrix elements of the Coulomb interaction is replaced by $V_{\mathbf{k}}(0f;f0) \to \bar{V}_{\mathbf{k}}(0f;f0) \equiv V_{\mathbf{k}}(0f;f0)/\eta^2$. The algebra simplifies considerably by rotating the photon polarization vectors such that one of them is perpendicular to $\boldsymbol{\mu}_{0f}$, so that this component has no interaction with the dipole (here the use of the sum rule in Sec. III pays off). We choose this to be the $\lambda = 2$ component. Note that this rotation is different for every level f, so that in the final results the inverse rotation needs to be applied in order not to lose generality. The following set of equations is now obtained:

$$\frac{1}{i}\frac{d}{dt}\hat{a}_{\mathbf{k}1} = -(\bar{\omega}_{\mathbf{k}} + 2D_{\mathbf{k}f})\hat{a}_{\mathbf{k}1} - 2D_{\mathbf{k}f}\hat{a}^{\dagger}_{-\mathbf{k}1} - iC_{\mathbf{k}f}(\hat{B}_{\mathbf{k}f} - \hat{B}^{\dagger}_{-\mathbf{k}f}) \tag{4.3a}$$

$$\frac{1}{i}\frac{d}{dt}\hat{B}_{\mathbf{k}f} = iC_{\mathbf{k}f}(\hat{a}_{\mathbf{k}1} + \hat{a}^{\dagger}_{-\mathbf{k}1}) - (\Omega_f + \bar{V}_{\mathbf{k}f})\hat{B}_{\mathbf{k}f} - \bar{V}_{\mathbf{k}f}\hat{B}^{\dagger}_{-\mathbf{k}f}, \tag{4.3b}$$

$$\frac{1}{i}\frac{d}{dt}\hat{a}_{\mathbf{k}2} = -\bar{\omega}_{\mathbf{k}}\hat{a}_{\mathbf{k}2}, \tag{4.3c}$$

with

$$C_{\mathbf{k}f} = \left(\frac{2\pi\rho}{\hbar\bar{\omega}_{\mathbf{k}}}\right)^{1/2}\Omega_f\mu^{\perp}_{0f}/\eta, \tag{4.4a}$$

$$D_{\mathbf{k}f} = \frac{2\pi\rho\Omega_f}{\hbar\bar{\omega}_{\mathbf{k}}}(\mu^{\perp}_{0f}/\eta)^2, \tag{4.4b}$$

$$\bar{V}_{\mathbf{k}f} = \bar{V}_{\mathbf{k}}(ff;00) = \bar{V}_{\mathbf{k}}(0f;f0). \tag{4.4c}$$

The transverse dipole moment is defined by $\boldsymbol{\mu}^{\perp}_{0f} \equiv (1 - \hat{\mathbf{k}}\hat{\mathbf{k}})\boldsymbol{\mu}_{0f}$, with $\hat{\mathbf{k}}$ the unit vector in the $\mathbf{k}$ direction. Equation (4.3c) trivially yields the "pure" photon polarized perpendicular to the plane through $\mathbf{k}$ and $\boldsymbol{\mu}_{0f}$, where the only material effect is contained in a modified velocity of light. Using Tyablikov's diagonalization procedure,[17-19,28] one obtains from Eqs. (4.3a) and (4.3b) two nontrivial polaritons as mixtures of a photon polarized in the plane through $\mathbf{k}$ and $\boldsymbol{\mu}_{0f}$ and of the exciton at wave vector $\mathbf{k}$ belonging to level f. We write for the annihilation operator of a polariton in branch $b (b = 1,2)$ belonging to level f:

$$\hat{\xi}_{\mathbf{k}fb} = w_{\mathbf{k}fb}\hat{a}_{\mathbf{k}1} + x_{\mathbf{k}fb}\hat{B}_{\mathbf{k}f} + y_{\mathbf{k}fb}\hat{a}^{\dagger}_{-\mathbf{k}1} + z_{\mathbf{k}fb}\hat{B}^{\dagger}_{-\mathbf{k}f}. \tag{4.5}$$

Imposing the condition

$$\frac{d\hat{\xi}_{\mathbf{k}fb}}{dt} = -i\omega_{\mathbf{k}fb}\hat{\xi}_{\mathbf{k}fb}, \tag{4.6}$$

the following eigenvalue problem is found from Eqs. (4.3a), (4.3b) and their Hermitian conjugates at $-\mathbf{k}$:

$$\begin{pmatrix} -\bar{\omega}_{\mathbf{k}} - 2D & iC & 2D & iC \\ -iC & -\Omega_f - \bar{V} & iC & \bar{V} \\ -2D & iC & \bar{\omega}_{\mathbf{k}} + 2D & iC \\ iC & -\bar{V} & -iC & \Omega_f + \bar{V} \end{pmatrix}\begin{pmatrix} w \\ x \\ y \\ z \end{pmatrix} = -\omega_{\mathbf{k}fb}\begin{pmatrix} w \\ x \\ y \\ z \end{pmatrix}, \tag{4.7}$$

where the subscripts $\mathbf{k}f$ on C, D, and $\bar{V}$, and $\mathbf{k}fb$ on w, x, y, and z have been suppressed for compactness. We have used $\bar{V}_{-\mathbf{k}f} = \bar{V}_{\mathbf{k}f}$, which holds for crystals with one molecule per unit cell. Equation (4.7) is symmetric with respect to inversion of $\mathbf{k}$, so that the coefficients w, x, y, and z also have this symmetry. The secular equation is quadratic in $\omega^2_{\mathbf{k}fb}$:

$$(\bar{\omega}^2_{\mathbf{k}} - \omega^2_{\mathbf{k}fb})(\Omega^2_f + 2\bar{V}_{\mathbf{k}f}\Omega_f - \omega^2_{\mathbf{k}fb}) - 4\pi\beta\Omega^2_f\omega^2_{\mathbf{k}fb} = 0, \tag{4.8}$$

with β defined by

$$4\pi\beta\Omega^2_f \equiv \frac{8\pi\rho\Omega_f}{\hbar}(\mu^{\perp}_{0f}/\eta)^2 = (f/\eta)^2, \tag{4.9}$$

where the last equality shows the connection to the notation

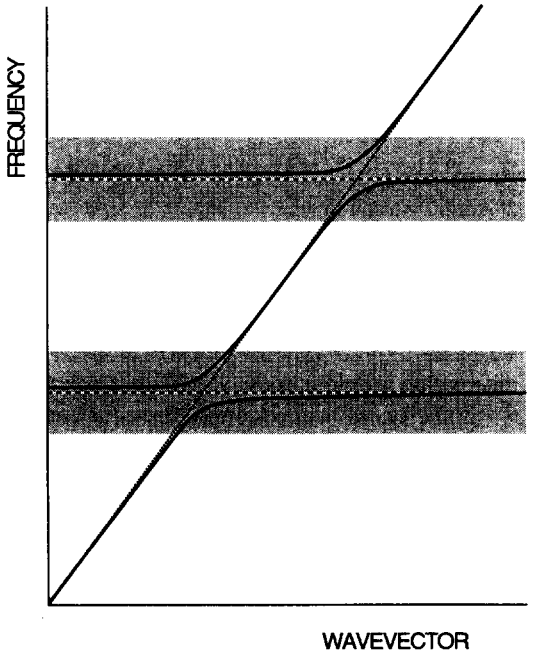

FIG. 1. Typical polariton dispersion diagram for a crystal of multilevel molecules. The level-by-level calculation of these curves given in the text yields good approximations in the shaded regions around the molecular (exciton) levels. In between these regions, the calculated curves smoothly join along the photon dispersion curve (dotted) with a background index of refraction, which, for clarity, has been assumed to be constant over the entire frequency region plotted.

of Ref. 4; f is the plasma frequency times the square root of the oscillator strength of the transition. We thus have

$$\omega_{\mathbf{k}fb}^2 = \tfrac{1}{2}[\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f + 4\pi\beta\Omega_f^2 + \overline{\omega}_k^2] \pm \tfrac{1}{2}\{[\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f + 4\pi\beta\Omega_f^2 + \overline{\omega}_k^2]^2 - 4\overline{\omega}_k^2(\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f)\}^{1/2}, \tag{4.10}$$

where the upper (lower) sign refers to the upper (lower) polariton branch belong to level f. The combination $\Omega_f(\Omega_f + 2\overline{V}_{\mathbf{k}f})$, which occurs several times in this expression, is the frequency squared of the exciton with wave vector $\mathbf{k}$.[8] The general features of the polariton dispersion curves Eq. (4.10) are well known and we will not discuss them here. The eigenvectors are found to be

$$w_{\mathbf{k}fb} = \mp \frac{(\overline{\omega}_{\mathbf{k}} + \omega_{\mathbf{k}fb})(\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f - \omega_{\mathbf{k}fb}^2)}{2(\overline{\omega}_{\mathbf{k}}\omega_{\mathbf{k}fb})^{1/2}[(\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f - \omega_{\mathbf{k}fb}^2)^2 + 4\pi\beta\Omega_f^2(\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f)]^{1/2}}, \tag{4.11a}$$

$$x_{\mathbf{k}fb} = \pm i\sqrt{\pi\beta}\,\frac{(\Omega_f + 2\overline{V}_{\mathbf{k}f} + \omega_{\mathbf{k}fb})\Omega_f^{3/2}}{\omega_{\mathbf{k}fb}^{1/2}[(\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f - \omega_{\mathbf{k}fb}^2)^2 + 4\pi\beta\Omega_f^2(\Omega_f^2 + 2\overline{V}_{\mathbf{k}f}\Omega_f)]^{1/2}}, \tag{4.11b}$$

$$y_{\mathbf{k}fb} = -\frac{\overline{\omega}_{\mathbf{k}} - \omega_{\mathbf{k}fb}}{\overline{\omega}_{\mathbf{k}} + \omega_{\mathbf{k}fb}} w_{\mathbf{k}fb}, \tag{4.11c}$$

$$z_{\mathbf{k}fb} = \frac{\Omega_f + 2\overline{V}_{\mathbf{k}f} - \omega_{\mathbf{k}fb}}{\Omega_f + 2\overline{V}_{\mathbf{k}f} + \omega_{\mathbf{k}fb}} x_{\mathbf{k}fb}. \tag{4.11d}$$

Again, the upper (lower) sign holds for the upper (lower) branch, and the coefficients are normalized according to[28]

$$|w_{\mathbf{k}fb}|^2 + |x_{\mathbf{k}fb}|^2 - |y_{\mathbf{k}fb}|^2 - |z_{\mathbf{k}fb}|^2 = 1 \tag{4.12}$$

The arbitrary phase factor has been chosen such that for both branches $w_{\mathbf{k}fb} = 1$ for frequencies far from Ω_f. Apart from our choice of the phase factor, Eqs. (4.11) reduce to Hopfield's expressions for the transformation coefficients if $\overline{V}$ is set equal to zero.[16] We furthermore note here, that often the polariton transformation is defined by starting from the exciton operators that diagonalize $\hat{H}_{\text{exc}}$. Only in the Heitler–London approximation will these operators be identical to our $\hat{B}_{\mathbf{k}f}$ and $\hat{B}_{\mathbf{k}f}^\dagger$.[8] This explains why our transformation has a slightly different form from the one found in, e.g., Ref. (18). Finally, it is useful for future reference to give the inverse transform, which is easily found along the lines presented in Ref. (28):

$$\hat{a}_{\mathbf{k}1} = \sum_b (w_{\mathbf{k}fb}^* \hat{\xi}_{\mathbf{k}fb} - y_{\mathbf{k}fb}\hat{\xi}^\dagger_{-\mathbf{k}fb}), \tag{4.13a}$$

$$\hat{B}_{\mathbf{k}f} = \sum_b (x_{\mathbf{k}fb}^* \hat{\xi}_{\mathbf{k}fb} - z_{\mathbf{k}fb}\hat{\xi}^\dagger_{-\mathbf{k}fb}), \tag{4.13b}$$

where * denotes complex conjugation.

V. POLARITON–PHONON SCATTERING

The inclusion of lattice vibrations as degrees of freedom adds extra terms to the material Hamiltonian. We will treat phonons in the standard way, and refer to Davydov[8] for a detailed explanation. As a consequence of the oscillation of the molecules around their equilibrium positions and orientations, the electronic ground state potential (van der Waals) energy of the crystal will not be a constant. This energy, together with the kinetic oscillation energy makes up the unperturbed phonon Hamiltonian

$$\hat{H}_{\text{ph}} = \sum_{\mathbf{q},j} \hbar\Omega_{\mathbf{q}j}\hat{b}_{\mathbf{q}j}^\dagger \hat{b}_{\mathbf{q}j}, \tag{5.1}$$

where $\hat{b}_{\mathbf{q}j}$ and $\hat{b}_{\mathbf{q}j}^\dagger$ are the annihilation and creation operators (obeying the usual Bose commutation relations) of a phonon of wave vector $\mathbf{q}$ in branch j, and $\Omega_{\mathbf{q}j}$ is the frequency of this phonon. The interaction between the phonons and the excitonic degrees of freedom is caused by the fluctuation of the intermolecular interaction matrix elements $V_{mn}(gg'ff')$ in Eq. (2.4) around their equilibrium value as a consequence of the varying intermolecular distances and orientations. Let $R_{m\alpha}(\alpha = 1,\ldots,6)$ denote the deviation of the translational and angular coordinates of molecule m from their equilibrium values. By expanding the intermolecular interaction to first order in the $R_{m\alpha}$, one finds, in addition to the equilibrium configuration intermolecular interactions, the linear exciton–phonon coupling, which in $\mathbf{k}$ space representation reads:

$$\hat{H}_{\text{ep}} = \frac{1}{\sqrt{N}} \sum_f \sum_{\mathbf{k},\mathbf{q},j} F_{jf}(\mathbf{k},\mathbf{q})\hat{B}_{\mathbf{k}+\mathbf{q},f}^\dagger \hat{B}_{\mathbf{k},f}(\hat{b}_{\mathbf{q}j} + \hat{b}^\dagger_{-\mathbf{q}j}), \tag{5.2}$$

with

$$F_{jk}(\mathbf{k},\mathbf{q}) = \sum_{m\neq n}\sum_{\alpha=1}^{6}\left(\frac{\hbar}{2I_\alpha\Omega_{\mathbf{q}j}}\right)^{1/2} e_{\mathbf{q}j}^\alpha \times\left\{\left[\frac{\partial}{\partial R_{n\alpha}} + e^{i\mathbf{q}\cdot\mathbf{r}_{mn}}\frac{\partial}{\partial R_{m\alpha}}\right]\hbar\overline{V}_{mn}(0f;f0)\right\}_{R=0} \tag{5.3}$$

Here I_α is the appropriate mass or moment of inertia for the αth degree of freedom and $e_{\mathbf{q}j}^\alpha$ is the αth component of the eigenvector of the dynamical matrix (from which the phonon branches are obtained) at the eigenvalue. $\Omega_{\mathbf{q}j}$. Several remarks are in place concerning Eq. (5.2). First, we assumed weak exciton–phonon coupling, so that the lattice deformation upon excitation can be neglected. Consistent with this assumption, we neglect the dispersion matrix elements which are due to the change of the van der Waals energy of a molecule with its surroundings when it is excited.

Furthermore, we restricted ourselves to the inclusion of the variation of the matrix elements $V_{mn}(0f;f0)$, in accordance with the approximations we made in the derivation of the polaritons in the previous section. Finally, we invoked, as is common, the Heitler–London approximation, which only introduces small errors in the exciton–phonon interaction which itself is already a perturbation. The total Hamiltonian is now given by

$$\hat{H} = \hat{H}_0 + \hat{H}_{\rm ph} + \hat{H}_{\rm ep}. \tag{5.4}$$

In order to take the effect of phonons on the susceptibilities into account, we could, of course, derive a new set of Heisenberg equations of motion by using the Hamiltonian Eq. (5.4), and take expectation values. Then, however, we would be forced to solve a huge coupled set of equations for the exciton and phonon variables in terms of the radiation field. This would be highly impractical, and moreover, unnecessary because we are only interested in the solutions to the exciton variables. Since at low temperature the coupling of the excitons and the photons is strong compared to the exciton–phonon coupling, the situation is ideally suited to apply a projection operator technique[27] which eliminates the phonon bath. This technique has been used before in a study of polariton desphasing in semiconductors by Takagahara.[22] We define the projection operator P by its action on the total density operator $\hat{\rho}(t)$ of the system

$$P\hat{\rho}(t) = \hat{\rho}_{\rm ph}^{T}\ {\rm Tr}_{\rm ph}\ \hat{\rho}(t), \tag{5.5}$$

where $\hat{\rho}_{\rm ph}^{T}$ denotes the density matrix of the phonons in thermodynamic equilibrium at temperature T, and ${\rm Tr}_{\rm ph}$ traces over the phonon degrees of freedom. Clearly, the reduced density operator $\hat{\sigma}(t) \equiv P\hat{\rho}(t)$ reproduces the exact expectations value of any exciton or radiation operator $\hat{O}$. Through standard manipulations,[27] one derives, starting from the Liouville equation, an exact reduced equation of motion for $\hat{\sigma}(t)$, from which the following equation for the expectation value $\langle \hat{O}(t) \rangle$ is obtained:

$$\frac{d}{dt}\langle \hat{O}(t)\rangle = -i \ll \hat{O}^{\dagger} | L\, | \hat{\sigma}(t) \gg - \int_{-\infty}^{t} dt' \ll \hat{O}^{\dagger} | L_{\rm ep} G(t,t') Q L_{\rm ep} | \hat{\sigma}(t') \gg, \tag{5.6}$$

$$G(t,t') = \exp[-i(L_0 + QL_{\rm ep})(t-t')]. \tag{5.7}$$

Here L is the Liouville operator associated with the total Hamiltonian, $\hbar L\hat{A} = [\hat{H},\hat{A}]$ ($\hat{A}$ arbitrary), and L_0 and $L_{\rm ep}$ are defined analogously; $Q = 1 - P$ stands for the complementary projection. Above, Liouville space notation has been used, whereby an arbitrary operator $\hat{A}$ is written as a ket $|\hat{A}\gg$, $\ll \hat{A}\,|\hat{B}\gg \equiv {\rm Tr}(\hat{A}^{\dagger}\hat{B})$ is the scalar product, and $\ll \hat{A} \mid L \mid \hat{B}\gg \equiv {\rm Tr}(\hat{A}^{\dagger} L \hat{B})$ is a Liouville space "matrix element".[29]

The calculation of the first term in Eq. (5.6), the mean field term, is straightforward. Using the hermitian character of the operator L in Liouville space, and the facts that $L_{\rm ep}$ is linear in the phonon creation and annihilation operators and that $\hat{\sigma}(t)$ is diagonal in the phonon operators, it is clear that this term exactly equals the expectation value of the Heisenberg equation of motion for $\hat{O}$ derived from the Hamiltonian $\hat{H}_0$. Thus, the mean field term of Eq. (5.6) reproduces, upon factorization of operator products, Eq. (3.6) for the exciton variables $\langle \hat{B}_{kfg}(t)\rangle$ (of course, the angular brackets now stand for the expectation value in the presence of phonons). The second right-hand side term of Eq. (5.6) (the "kernel" term) formally contains the exact corrections due to interactions with the phonon bath. In practice, however, calculation of this term is impossible, and one has to resort to a perturbation expansion around the unperturbed propagator $G_0(t,t') \equiv \exp(-iL_0 t)$, using $L_{\rm ep}$ as the perturbation. Since G_0 is the propagator of the coupled photon–exciton system, it is clear that polaritons (and thus the equations of motion for the radiation field) play an explicit role in the derivation of the equations for the exciton variables.

Before discussing the perturbation expansion, it is useful to consider the equations of motion for the radiation field. As mentioned in Sec. III, the Heisenberg equations of motion for $\hat{a}_{k\lambda}$ and $\hat{a}_{k\lambda}^{\dagger}$ are exactly equivalent to the Maxwell equations (since these equations do not contain operator products, there is no need to invoke the factorization approximation). Any contribution from the kernel term to the equation of motion for $\langle \hat{a}_{k\lambda}(t)\rangle$ or $\langle \hat{a}_{k\lambda}^{\dagger}(t)\rangle$, would destroy the equivalence, and introduce unphysical damping terms to the Maxwell equations. It is easily shown, however, that the kernel term for radiation operators vanishes. To this end, one exploits the fact that $L_{\rm ep}$ is hermitian in Liouville space, so that $\ll \hat{O}^{\dagger} | L_{\rm ep} G(t,t') Q L_{\rm ep} | \hat{\sigma}(t') \gg = \ll L_{\rm ep}\hat{O}^{\dagger} | G(t,t') Q L_{\rm ep} | \hat{\sigma}(t') \gg$. Since $H_{\rm ep}$ does not contain radiation operators (there is no direct interaction between radiation field and phonons), $L_{\rm ep}\hat{O}^{\dagger}$ rigorously vanishes for an arbitrary operator $\hat{O}$. Thus, even if we allow the presence of a phonon bath, our equations for the radiation fields are still exactly equivalent with the Maxwell equations.

We now turn to the calculation of the kernel term for the exciton variables. We confine ourselves to the lowest order term in the perturbation expansion, so that $G(t,t')$ in Eq. (5.6) is replaced by $G_0(t,t')$. Since $G_0(t,t')$ propagates polaritons, it is natural to work with polariton variables. Thus, we first evaluate the kernel term for the polaritons ($\langle \hat{\xi}_{kfb}(t)\rangle$) and later on transform this to the kernel term for the excitons. Now, the interaction Hamiltonian [Eq. (5.2)] has to be expressed in polariton operators by invoking the transformation Eq. (4.13b). This generates many interaction terms, so that the kernel term contains many contributions. A considerable reduction in complexity may be achieved, however, by making the common approximation that the transformation coefficient $z_{kfb} = 0$.[19,25] In view of Eq. (4.11d), this approximation is reasonable for polariton frequencies close to the exciton frequency, which is the usual region of interest. From the quantitative analysis of the transformation coefficients given in Sec. VII for a specific application, it may be seen that, indeed, over a wide range of the polariton dispersion curve z may safely be neglected. We now have

$$\hat{H}_{\rm ep} \approx \frac{1}{\sqrt{N}} \sum_f \sum_{\mathbf{k},\mathbf{q},j} F_{jf}(\mathbf{k},\mathbf{q}) \times \sum_{b,b'} x_{\mathbf{k}+\mathbf{q},fb} x^*_{\mathbf{k}fb'} \hat{\xi}^\dagger_{\mathbf{k}+\mathbf{q},fb} \hat{\xi}_{\mathbf{k}fb'} (b_{\mathbf{q}j} + b^\dagger_{-\mathbf{q}j}). \quad (5.8)$$

In Appendix A it is shown that by using this interaction, the kernel term for the polaritons reads in the Markov approximation

$$\left(\frac{d\langle \hat{\xi}_{\mathbf{k}fb}(t)\rangle}{dt}\right)_{\rm ph} = \frac{-\pi x_{\mathbf{k}fb}}{\hbar^2 N} \sum_{\mathbf{q},j} |F_{jf}(\mathbf{k},\mathbf{q})|^2 \sum_{b',b''} |x_{\mathbf{k}+\mathbf{q},fb'}|^2 x^*_{\mathbf{k}fb''} \times \{\langle n_{\mathbf{q}j}\rangle_T \delta(\Omega_{\mathbf{q}j} - \omega_{\mathbf{k}+\mathbf{q},fb'} + \omega_{\mathbf{k}fb''}) + \langle n_{-\mathbf{q}j} + 1\rangle_T \delta(\Omega_{-\mathbf{q}j} + \omega_{\mathbf{k}+\mathbf{q},fb'} - \omega_{\mathbf{k}fb''})\} \times \langle \hat{\xi}_{\mathbf{k}fb''}(t)\rangle. \quad (5.9)$$

The equation for $\langle \hat{\xi}^\dagger_{\mathbf{k}fb}(t)\rangle$ is, of course, obtained by complex conjugation. $\langle n_{\mathbf{q}j}\rangle_T$ denotes the equilibrium occupation number of phonons of wave vector $\mathbf{q}$ in branch j at temperature T. The first term in curly brackets reflects absorption of a phonon by the initial polariton at frequency $\omega_{\mathbf{k}fb''}$, whereas the second term reflects emission. Neglecting interbranch scattering, the dephasing rate of the polariton implied by Eq. (5.9) agrees with the scattering frequency as obtained in, e.g., Ref. 19. Equation (5.9) may alternatively be obtained by application of the Fermi golden rule. In the derivation of the kernel term, we have approximated the contribution of the Hamiltonian H_0 relevant to the level f as $\Sigma_{\mathbf{k}b} \omega_{\mathbf{k}fb} \hat{\xi}^\dagger_{\mathbf{k}fb} \hat{\xi}_{\mathbf{k}fb}$ and used the Bose commutation relations $[\hat{\xi}_{\mathbf{k}fb}, \hat{\xi}_{\mathbf{k}'fb'}] = \delta_{\mathbf{k}\mathbf{k}'}\delta_{bb'}$. This linearization is necessary because it is otherwise difficult to evaluate $G_0(t,t')$ explicity. The mean field term, however, will be kept as in Sec. III, i.e., derived from the full Hamiltonian H_0 without inferring the boson approximation. Since the kernel term is a correction to the main equations of motion provided by the mean field term, we argue that making the boson approximation in the kernel does not introduce significant errors in the final results.

The kernel term for the exciton operator $\hat{B}_{\mathbf{k}f}$ is obtained from Eq. (5.9) by applying the polariton transformation Eqs. (4.5) and (4.13b), where, consistent with the approximation above, $z_{\mathbf{k}fb}$ is set equal to zero. The resulting expression contains the expectaton values $\langle \hat{a}_{\mathbf{k}1}(t)\rangle$ and $\langle \hat{a}^\dagger_{-\mathbf{k}1}(t)\rangle$, which may be rewritten in terms of $\langle \hat{\mathbf{E}}(\mathbf{k},t)\rangle$ and $\langle \hat{\mathbf{A}}(\mathbf{k},t)\rangle$, after the photon polarization vectors have been rotated back to their original orientations (cf. Sec. IV). We then arrive at

$$\left(\frac{d\langle \hat{B}_{\mathbf{k}f}(t)\rangle}{dt}\right)_{\rm ph} = -\Gamma_{1f}(\mathbf{k})\langle \hat{B}_{\mathbf{k}f}(t)\rangle - \frac{i}{\sqrt{N}}\Gamma_{2f}(\mathbf{k})\boldsymbol{\mu}_{0f}\cdot\langle \hat{\mathbf{A}}(\mathbf{k},t)\rangle - \frac{1}{\sqrt{N}}\Gamma_{3f}(\mathbf{k})\boldsymbol{\mu}_{0f}\cdot\langle \hat{\mathbf{E}}(\mathbf{k},t)\rangle, \quad (5.10)$$

with

$$\Gamma_{1f}(\mathbf{k}) = \frac{\pi}{\hbar^2 N} \sum_{\mathbf{q},j} |F_{jf}(\mathbf{k},\mathbf{q})|^2 \sum_{b,b'} |x_{\mathbf{k}+\mathbf{q},fb'}|^2 |x_{\mathbf{k}fb}|^2 \times \{\langle n_{\mathbf{q}j}\rangle_T \delta(\Omega_{\mathbf{q}j} - \omega_{\mathbf{k}+\mathbf{q},fb'} + \omega_{\mathbf{k}fb}) + \langle n_{-\mathbf{q}j} + 1\rangle_T \delta(\Omega_{-\mathbf{q}j} + \omega_{\mathbf{k}+\mathbf{q},fb'} - \omega_{\mathbf{k}fb})\} \quad (5.11a)$$

$$\Gamma_{2f}(\mathbf{k}) = \frac{\pi}{\hbar^2 N}\left(\frac{\bar{\omega}_{\mathbf{k}}\rho}{2\pi\hbar c^2 \mu^2_{0f}}\right)^{1/2} \sum_{\mathbf{q}} |F_{jf}(\mathbf{k},\mathbf{q})|^2 \times \sum_{b,b'} |x_{\mathbf{k}+\mathbf{q},fb'}|^2 \frac{1}{2i} x^*_{\mathbf{k}fb}(w_{\mathbf{k}fb} + y_{\mathbf{k}fb})\{\cdots\}, \quad (5.11b)$$

$$\Gamma_{3f}(\mathbf{k}) = \frac{\pi}{\hbar^2 N}\left(\frac{\rho}{2\pi\hbar\bar{\omega}_k \mu^2_{0f}}\right)^{1/2} \sum_{\mathbf{q}j} |F_{jf}(\mathbf{k},\mathbf{q})|^2 \times \sum_{b,b'} |x_{\mathbf{k}+\mathbf{q},fb'}|^2 \frac{1}{2i} x^*_{\mathbf{k}fb}(w_{\mathbf{k}fb} - y_{\mathbf{k}fb})\{\cdots\}. \quad (5.11c)$$

In Eqs. (5.11b) and (5.11c), $\{\cdots\}$ stands for the factor in curly brackets occurring in Eq. (5.11a). In the derivation of these relaxation constants we have used the relation $\Sigma_b |x_{\mathbf{k}fb}|^2 = 1$, which stems from one of the normalization conditions[28] for the transformation coefficients $[\Sigma_b(|x_{\mathbf{k}fb}|^2 - |z_{\mathbf{k}fb}|^2) = 1]$, with the approximation $z_{\mathbf{k}fb} = 0$. We note that all $\Gamma_{if}(\mathbf{k})$ $(i = 1,2,3)$ are real quantities. Had we neglected the microscopic retardation effects and used the *exciton* propagator for $G_0(t,t')$ instead of the *polariton* propagator, we would have obtained an entirely different relaxation equation for $\langle \hat{B}_{\mathbf{k}f}(t)\rangle$ than the one above. First, the terms proportional to the radiation fields would not have been present in that case, and second the relaxation constant $\Gamma_{1f}(\mathbf{k})$ would not have contained $\Sigma_{bb'} |x_{\mathbf{k}+\mathbf{q},fb'}|^2 |x_{\mathbf{k}fb}|^2$ and, more importantly, would have had exciton frequencies in the energy conserving δ functions instead of polariton frequencies.[8,19] Both differences will affect the susceptibilities.

So far, we have only considered the damping of $\langle \hat{B}_{\mathbf{k}0f}\rangle$ $(= \langle \hat{B}_{\mathbf{k}f}(t)\rangle)$. From this the damping of $\langle \hat{B}_{\mathbf{k}f0}(t)\rangle = \langle \hat{B}_{-\mathbf{k}f}(t)\rangle^*$ follows trivially by complex conjugation. We will assume that $\Gamma_{if}(-\mathbf{k}) = \Gamma_{if}(\mathbf{k})$ $(i = 1,2,3)$, which holds if $\Omega_{-\mathbf{q}j} = \Omega_{\mathbf{q}j}$. It is, in principle, also possible to evaluate the kernel term for $\langle \hat{B}_{\mathbf{k}fg}(t)\rangle$ with both $f \neq 0$ and $g \neq 0$, by taking in Eq. (5.6)

$$\hat{O} = \hat{B}_{\mathbf{k}fg} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}'} \hat{B}_{\mathbf{k}'f0} \hat{B}_{-\mathbf{k}'0g}.$$

Clearly, the result will be very convoluted, and at present we will confine ourselves to the inclusion of damping of coherences between the ground state and an excited state. This is sufficient to describe the large class of nonlinear optical experiments in which a resonant multiphoton transition between ground state and an excited state is probed. Combining the exciton damping equations with Eq. (3.6) and using the Fourier transform [Eq. (2.16c)], we obtain as total equations of motion in $(\mathbf{k},\omega)$ space

$$
\begin{aligned}
&-i\omega\langle\hat{B}_{\mathbf{k}fg}(\omega)\rangle \\
&\quad = i\Omega_{fg}\langle\hat{B}_{\mathbf{k}fg}(\omega)\rangle \\
&\qquad + \frac{i}{2\pi\sqrt{N}}\sum_{\substack{\mathbf{k}'\\ 1\mathrm{BZ}}}\int d\omega' \sum_{f',g'}\langle\hat{B}_{\mathbf{k}f'g'}(\omega')\rangle \sum_{h}\left[V_{\mathbf{k}'}(hf';fg')\langle\hat{B}_{\mathbf{k}-\mathbf{k}',hg}(\omega-\omega')\rangle - V_{\mathbf{k}'}(gf';hg')\langle\hat{B}_{\mathbf{k}-\mathbf{k}',fh}(\omega-\omega')\rangle\right] \\
&\qquad - \frac{i}{\hbar}\frac{1}{2\pi V}\sum_{\mathbf{k}'}\int d\omega' \frac{\hat{\mathbf{E}}(\mathbf{k}',\omega')}{\omega'}\cdot\sum_{h}\left[\boldsymbol{\mu}_{hf}\Omega_{hf}\langle\hat{B}_{\mathbf{k}-\mathbf{k}',hg}(\omega-\omega')\rangle - \boldsymbol{\mu}_{gh}\Omega_{gh}\langle\hat{B}_{\mathbf{k}-\mathbf{k}',fh}(\omega-\omega')\rangle\right] \\
&\qquad - \delta_{g0}(1-\delta_{f0})\left[\Gamma_{1f}(\mathbf{k})\langle\hat{B}_{\mathbf{k}f0}(\omega)\rangle - \frac{c}{\omega\sqrt{N}}\Gamma_{2f}(\mathbf{k})\boldsymbol{\mu}_{0f}\cdot\langle\hat{\mathbf{E}}(\mathbf{k},\omega)\rangle + \frac{1}{\sqrt{N}}\Gamma_{3f}(\mathbf{k})\boldsymbol{\mu}_{0f}\cdot\langle\hat{\mathbf{E}}(\mathbf{k},\omega)\rangle\right] \\
&\qquad - \delta_{f0}(1-\delta_{g0})\left[\Gamma_{1g}(\mathbf{k})\langle\hat{B}_{\mathbf{k}0g}(\omega)\rangle + \frac{c}{\omega\sqrt{N}}\Gamma_{2g}(\mathbf{k})\boldsymbol{\mu}_{0g}\cdot\langle\hat{\mathbf{E}}(\mathbf{k},\omega)\rangle + \frac{1}{\sqrt{N}}\Gamma_{3g}(\mathbf{k})\boldsymbol{\mu}_{0g}\cdot\langle\hat{\mathbf{E}}(\mathbf{k},\omega)\rangle\right]. \qquad (5.12)
\end{aligned}
$$

Equation (5.12) constitutes a set of nonlinear equations for the electronic variables $\langle\hat{B}_{\mathbf{k}fg}(\omega)\rangle$ in which microscopic retardation effects are properly incorporated. As explained in Sec. III, the susceptibilities are obtained from these equations by iteratively solving them in powers of the electric field.

VI. LINEAR AND SECOND ORDER SUSCEPTIBILTIES

In this section, we present explicit results for the linear ($\chi^{(1)}$) and second order ($\chi^{(2)}$) susceptibilities as obtained from Eq. (5.12). First, however, we establish our notation.[2] The expectation value of the Maxwell electric field is assumed to contain a few discrete Fourier components with amplitudes $\mathbf{E}(\mathbf{k}_i,\omega_i)$:

$$\langle\hat{\mathbf{E}}(\mathbf{r},t)\rangle = \sum_i \mathbf{E}(\mathbf{k}_i,\omega_i)e^{i(\mathbf{k}_i\mathbf{r}-\omega_i t)}. \qquad (6.1)$$

The Fourier transform of this field, in terms of which Eq. (5.12) is formulated, is

$$\langle\hat{\mathbf{E}}(\mathbf{k},\omega)\rangle = 2\pi V\sum_i \mathbf{E}(\mathbf{k}_i,\omega_i)\delta_{\mathbf{k},\mathbf{k}_i}\delta(\omega-\omega_i). \qquad (6.2)$$

As the total field $\langle\hat{\mathbf{E}}(\mathbf{r},t)\rangle$ is real, the Fourier components in Eq. (6.1) always come in pairs; for every $(\mathbf{k}_i,\omega_i)$ component there is a counterpart at $(-\mathbf{k}_i,-\omega_i)$ with amplitude $[\mathbf{E}(\mathbf{k}_i,\omega_i)]^*$. In analogy, $\mathbf{P}(\mathbf{k},\omega)$ denotes the discrete Fourier amplitude of the expectation value of the polarization field at wave vector $\mathbf{k}$ and frequency ω. It is common to define the susceptibilities as the expansion coefficients of $\mathbf{P}(\mathbf{k},\omega)$ in terms of the $\mathbf{E}(\mathbf{k}_i,\omega_i)$, and explicitly we write:

$$\mathbf{P}(\mathbf{k},\omega) = \mathbf{P}^{(1)}(\mathbf{k},\omega) + \mathbf{P}^{(2)}(\mathbf{k},\omega) + \cdots \qquad (6.3)$$

with

$$\mathbf{P}^{(1)}(\mathbf{k},\omega) = \sum_i \chi^{(1)}(-\mathbf{k}-\omega;\mathbf{k}_i\omega_i)\cdot\mathbf{E}(\mathbf{k}_i,\omega_i), \qquad (6.4a)$$

$$\mathbf{P}^{(2)}(\mathbf{k},\omega) = \sum_{ij}\chi^{(2)}(-\mathbf{k}-\omega;\mathbf{k}_i\omega_i,\mathbf{k}_j\omega_j):\mathbf{E}(\mathbf{k}_i,\omega_i)\mathbf{E}(\mathbf{k}_j,\omega_j), \quad \text{etc.} \qquad (6.4b)$$

The nth order susceptibility $\chi^{(n)}$ is a tensor of rank $n+1$, and the indices $i, j, \ldots$ run over all modes, subject to the conditions $\mathbf{k} = \mathbf{k}_i + \mathbf{k}_j + \cdots$ and $\omega = \omega_i + \omega_j + \cdots$.

It is useful to note at this point, that the set $\mathbf{E}(\mathbf{k}_i,\omega_i)$ does not only contain the components of the electric field due to the linear propagation of the incoming laser fields in the sample, but also all components nonlinearly generated from these, up to the order that one is interested in. For example, in a sum-frequency generation of two laser fields at $(\mathbf{k}_1,\omega_1)$ and $(\mathbf{k}_2,\omega_2)$, also $(\mathbf{k}_3,\omega_3)\equiv(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$ is explicitly included in the set $(\mathbf{k}_i,\omega_i)$. According to Eq. (6.4a) there is, thus, a linear polarization component related to $\mathbf{E}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$. Even though this is counterintuitive (because one is inclined to think of $\mathbf{E}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$ as a second order field), this is perfectly in order, since this polarization component guarantees that the sum signal propagates with the correct index of refraction. This picture, in which all electric field amplitudes are regarded as being of first order, is common, and intimately related to the fact that the susceptibilities are defined with respect to the total Maxwell electric field instead of the external field. In the practical implementation, however, one must keep in mind that due to this ordering the nonlinear component $\mathbf{P}^{(n)}(\mathbf{k},\omega)$ ($n\geqslant 2$) contains contributions which are of higher order in the laser field amplitudes than n (cascading).[2,12]

The iteration of the equations of motion is carried out in Appendix B and yields for the linear susceptibility:

$$
\begin{aligned}
\chi^{(1)}(-\mathbf{k}-\omega;\mathbf{k}\omega) &= \sum_f \frac{2\rho\hbar^{-1}\Omega_f\,\boldsymbol{\mu}_{0f}\boldsymbol{\mu}_{f0}}{-[\omega+i\Gamma_{1f}(\mathbf{k})]^2+\Omega_f(\Omega_f+2\bar{V}_{\mathbf{k}f})} \\
&\quad\times[1+c_f(\mathbf{k},\omega)+d_f(\mathbf{k},\omega)i] \qquad (6.5)
\end{aligned}
$$

with

$$c_f(\mathbf{k},\omega) = -\frac{\hbar}{\rho\Omega_f}\Gamma_{1f}(\mathbf{k})\Gamma_{3f}(\mathbf{k})$$

and

$$d_f(\mathbf{k},\omega) = \frac{\Gamma_{1f}(\mathbf{k})}{\omega} + \frac{\hbar\omega}{\rho\Omega_f}\Gamma_{3f}(\mathbf{k}) + \frac{\hbar c}{\rho\omega}\Gamma_{2f}(\mathbf{k}). \qquad (6.6)$$

For the second order susceptibility we find

$$\chi^{(2)}(-\mathbf{k}_1-\mathbf{k}_2-\omega_1-\omega_2;\mathbf{k}_1\omega_1,\mathbf{k}_2\omega_2)$$
$$=-\frac{1}{2!}\sum_{\mathscr{P}}\frac{2\rho}{\hbar^2}\sum_{f,g}\mu_{0g}\mu_{gf}\mu_{f0}\frac{\Omega_f\Omega_{fg}}{\omega_1\omega_2}[\omega_1(\omega_1+\omega_2)+\Omega_g(\Omega_f+2\overline{V}_{\mathbf{k}_1 f})]I_{0g}(\omega_1+\omega_2,\mathbf{k}_1+\mathbf{k}_2)I_{0f}(\omega_1,\mathbf{k}_1)$$
$$+\frac{1}{2!}\sum_{\mathscr{P}}\frac{2\rho}{\hbar^2}\sum_{f,g}\mu_{fg}\mu_{g0}\mu_{0f}\frac{\Omega_f\Omega_g}{\omega_1\omega_2}[\omega_1(\omega_1+\omega_2)+\Omega_{fg}(\Omega_f+2\overline{V}_{\mathbf{k}_1 f})+\{\omega_1\omega_2\Omega_{fg}+(\omega_1+\omega_2)\omega_2(\Omega_f+2\overline{V}_{\mathbf{k}_1 f})\}$$
$$\times\overline{V}_{\mathbf{k}_2 g}I_{0g}(\omega_2,\mathbf{k}_2)]I_{fg}(\omega_1+\omega_2)I_{0f}(\omega_1,\mathbf{k}_1), \tag{6.7}$$

with

$$I_{0f}(\omega,\mathbf{k})=[-[\omega+i\Gamma_{1f}(\mathbf{k})]^2+\Omega_f(\Omega_f+2\overline{V}_{\mathbf{k}f})]^{-1} \tag{6.8a}$$

$$I_{fg}(\omega,\mathbf{k})=[-\omega^2+\Omega_{fg}^2]^{-1}. \tag{6.8b}$$

In Eq. (6.7) $\mathscr{P}$ stands for permutation of ω_1 and ω_2 (also in the degenerate case $\omega_1=\omega_2$) and simultaneous permutation of the dipole moments μ_{gf} and μ_{f0} in the first term and μ_{g0} and μ_{0f} in the second term.

We next analyze these susceptibilities. We first note that the iteration has been carried out making the approximation that only interaction matrix elements of the form $V_{\mathbf{k}}(gf;fg)$ and $V_{\mathbf{k}}(gg;ff)$ occur, which are rescaled by a background dielectric constant ($V\to\overline{V}\equiv V/\eta^2$) (cf. Sec. IV and Appendix B). Formally, it is also possible to evaluate the susceptibilities when relaxing this assumption; the calculation of $\chi^{(1)}$ and $\chi^{(2)}$ would then involve the inversion of a $K\times K$ and a $K(K-1)/2\times K(K-1)/2$ matrix, respectively, where K is the number of molecular excited states. We now focus on $\chi^{(1)}$ in more detail. Its denominator shows the usual resonances at the exciton frequencies $[\Omega_f(\Omega_f+2\overline{V}_{\mathbf{k}f})]^{1/2}$ at wave vector $\mathbf{k}$. One often writes[10]

$$\Omega_f(\Omega_f+2\overline{V}_{\mathbf{k}f})=\overline{\Omega}_f^2+\frac{\hbar\overline{\Omega}_f k^2}{m_f^*}, \tag{6.9}$$

with $\overline{\Omega}_f$ the $\mathbf{k}=0$ frequency of the exciton related to the fth molecular level and m_f^* its effective mass. For dipolar interactions, these parameters may be written[14(b),30]

$$\overline{\Omega}_f^2=\Omega_f\left[\Omega_f+\frac{16\pi}{3}\frac{\rho\mu_{0f}^2}{\hbar\eta^2}P_2(\hat{\mu}_{0f}\cdot\hat{\mathbf{k}})\right], \tag{6.10a}$$

$$\frac{1}{m_f^*}=-\frac{8\pi}{15}\frac{\Omega_f}{\overline{\Omega}_f}\frac{\rho\mu_{0f}^2}{\hbar^2\eta^2}R_c^2P_2(\hat{\mu}_{0f}\cdot\hat{\mathbf{k}}), \tag{6.10b}$$

where $P_2(x)=(3x^2-1)/2$, $\hat{\mu}_{0f}$ and $\hat{\mathbf{k}}$ denote unit vectors along μ_{0f} and $\mathbf{k}$, and R_c is of the order of the lattice constant. Furthermore, the broadening of the resonances in $\chi^{(1)}$ is given by $\Gamma_{1f}(\mathbf{k})$. [cf. Eq. (5.11a)], which clearly contains information on the polaritons and does *not* represent the exciton dephasing rate (i.e., the relaxation rate obtained by taking the exciton propagator for $G_0(t,t')$ in Sec. V) as is commonly assumed. Linear optical experiments, however, necessarily probe frequencies very close to the exciton frequencies, so that the polaritons which are relevant in such experiments are almost pure excitons and the observed damping rate will be indistinguishable from the exciton damping rate (see Sec. VII). Finally, the numerator in Eq. (6.5) differs from the usual form in the occurrence of the real quantities $c_f(\mathbf{k},\omega)$ and $d_f(\mathbf{k},\omega)$, which are mainly due to the damping of $\langle\hat{B}_{\mathbf{k}f}(t)\rangle$ proportional to the electromagnetic fields. We note that $\Gamma_{2f}(\mathbf{k})$ and $\Gamma_{3f}(\mathbf{k})$ both contain the transformation coefficients $w_{\mathbf{k}fb}$ and $y_{\mathbf{k}fb}$, which for linear optical experiments are small, because, as explained above, the photonic part in polaritons created in such experiments is very small. Since, moreover, $\Gamma_{1f}(\mathbf{k})/\omega\ll 1$ for realistic cases, the effect of $c_f(\mathbf{k},\omega)$ and $d_f(\mathbf{k},\omega)$ on the linear optics is insignificant. The presence of these quantities in $\chi^{(1)}$ will be more important, however, in the linear propagation of nonlinearly generated signals. A more quantitative analysis for a specific experiment is given in Sec. VII.

We now turn to $\chi^{(2)}$. First, it is easily shown that if the intermolecular interaction is completely neglected (all $\overline{V}_{\mathbf{k}f}=0$) and the damping is ignored, Eq. (6.7) indeed reduces to the molecular number density times the second order molecular hyperpolarizability, which is in the minimal coupling ($\mathbf{p}\cdot\mathbf{A}$) Hamiltonian given by

$$\beta(-\omega_1-\omega_2;\omega_1,\omega_2)$$
$$=-\frac{1}{2!}\sum_{\mathscr{P}}\frac{1}{\hbar^2}\sum_{f,g}\mu_{0g}\mu_{gf}\mu_{f0}\frac{\Omega_f\Omega_{fg}}{\omega_1\omega_2}\left[\frac{1}{(\omega_1+\omega_2-\Omega_g)(\omega_1-\Omega_f)}+\frac{1}{(\omega_1+\omega_2+\Omega_g)(\omega_1+\Omega_f)}\right]$$
$$+\frac{1}{2!}\sum_{\mathscr{P}}\frac{1}{\hbar^2}\sum_{f,g}\mu_{fg}\mu_{g0}\mu_{0f}\frac{\Omega_f\Omega_g}{\omega_1\omega_2}\left[\frac{1}{(\omega_1+\omega_2-\Omega_{fg})(\omega_1-\Omega_f)}+\frac{1}{(\omega_1+\omega_2+\Omega_{fg})(\omega_1+\Omega_f)}\right]. \tag{6.11}$$

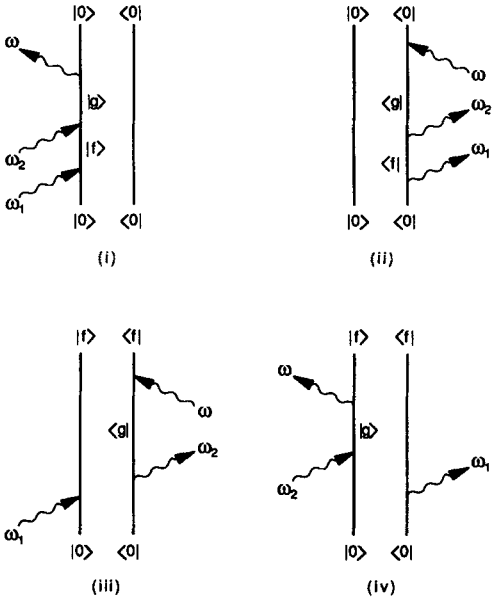

FIG. 2. The double-sided Feynman diagrams contributing to the second order molecular polarizability ($\omega = \omega_1 + \omega_2$). Diagrams (i) through (iv) correspond to the successive terms in Eq. (6.11). There are four more diagrams which only differ from those shown by permutation of ω_1 and ω_2.

The double-sided Feynman diagrams[3] contributing to this expression are shown in Fig. 2. Second, we remark that in the present approximation $\chi^{(2)}$ is *not* of the form predicted by the local field approach, where it would be given by a product of β and well-defined local field correction factors.[3,7] Third, as in the linear case, it is formally clear that the width of the nonlinear optical line shape [$\Gamma_{1f}(\mathbf{k})$] is affected by polaritons. In contrast to the linear experiments, however, these polariton effects may be very pronounced in nonlinear optical experiments, because of the much larger admixtures of photons into the polaritons which usually play a role in them. This is a consequence of the flexibility which one has to choose the wavevector of the coherently created nonlinear signal (phase matching).[4,19] Finally, we mention that in the derivation of $\chi^{(2)}$ we were mainly interested in the resonance structure. We therefore neglected the role of $\Gamma_{2f}(\mathbf{k})$ and $\Gamma_{3f}(\mathbf{k})$ completely. In a more complete form of $\chi^{(2)}$, corrections involving the $c_f(\mathbf{k}_i,\omega_i)$ and $d_f(\mathbf{k}_i,\omega_i)$ for $i = 1,2$ [Eq. (6.6)] would occur (cf. Sec. VII).

VII. DISCUSSION

In this paper, we developed a scheme for the microscopic calculation of nonlinear optical susceptibilities in condensed phases based on the iterative solution of reduced equations of motion for the excitonic variables in powers of the Maxwell electric field. There are several advantages to our approach. First, the intermolecular interactions can be incorporated without diagonalizing the material Hamiltonian, so that the application is not restricted to the perfect crystal case considered here, but is readily extendable to disordered systems, like mixed crystals, glasses, and dense solutions. Second, since we work directly with the Maxwell (internal) electric field, there is no need to make the cumbersome conversion from the external to the internal field, as is for example necessary when applying linear and nonlinear response theory. Third, other material degrees of freedom than the electronic ones, may readily be incorporated in an equation-of-motion approach by using projection operator techniques. Finally, our method does not rely upon the Bose approximation for the excitons or the polaritons; only in the explicit calculation of the polariton dephasing rates has this approximation been used.

Although, in principle, our approach may be applied to any scattering mechanism, we have analyzed in particular the effect of phonons on the nonlinear susceptibilities of low temperature pure crystals, in which the coupling between the excitons and the transverse radiation field is stronger than the exciton–phonon coupling. In that case, the elementary crystal excitations which are damped by the phonons are the polaritons, and not the excitons. As we have shown, this implies that the susceptibilities cannot be viewed as purely material quantities, because their calculation requires explicit incorporation of the transverse radiation field. Our results for $\chi^{(1)}$ and $\chi^{(2)}$ clearly show deviations from their usual forms due to these microscopic polariton effects. Moreover, it is clear from our expression (6.5) for $\chi^{(1)}$ that in general it is not sufficient to account for polariton scattering processes by just replacing the exciton dephasing rate in the denominator by the polariton dephasing rate, as has been suggested by several authors.[22–24]

Clear evidence for the importance of microscopic retardation effects has recently been provided by Small and coworkers.[4] They measured the one-photon absorption (OPA), second-harmonic generation (SHG) and two-photon excited fluorescence (TPE) profiles in pure strain-free naphthalene crystals at low temperatures. OPA is a linear optical process, in which Im $\chi^{(1)}$ is observed, whereas SHG and TPE are nonlinear processes with signals proportional to $|\chi^{(2)}|^2$ and Im $\chi^{(3)}$, respectively.[31] All experiments were done in resonance with the **a** exciton at $\bar{\Omega}_a = 31\,475\ \mathrm{cm}^{-1}$. It was found that the width of the lines observed in the linear and nonlinear experiments differed by roughly one order of magnitude and, moreover, had entirely different temperature dependencies. Traditionally, this width is interpreted as the dephasing rate of the exciton, which makes it impossible to understand this discrepancy. Namely, even though the linear and nonlinear experiments involve excitons at different wave vectors (phase matching), the dispersion of excitons in aromatic crystals is too weak to explain such a difference in their damping rates. The polaritons, however, have a much more pronounced dispersion in the region of interest, and, therefore, Small and co-workers made the ad hoc conjecture that the observed width is actually the damping rate of the polaritons at the wavevector relevant to the specific experiment.

Our microscopic calculation shows that for low temperature crystals the widths of optical lines indeed involve the polariton dispersion curves rather than the exciton dispersion curve. Let us have a closer look at the form of our $\chi^{(1)}$ and $\chi^{(2)}$ for the specific experimental set up of Small and coworkers. In the OPA measurements, the laser is tuned close to the frequency of the **a** exciton, and, neglecting spatial dis-

persion, the linear susceptibility Eq. (6.5) may then be written

$$\chi^{(1)}(-\omega;\omega)=\chi_{\rm nr}^{(1)}+\frac{\rho}{\hbar}\frac{\mu_{0a}\mu_{a0}}{\bar{\Omega}_a-\omega-i\Gamma_{1a}^{lin}}, \tag{7.1}$$

where $\chi_{\rm nr}^{(1)}$ is the nonresonant contribution due to the other electronic transitions, $\bar{\Omega}_a$ is the frequency of the **a** exciton, orginating from the molecular level at $\Omega_a = 32\,020\ {\rm cm}^{-1}$, and Γ_{1a}^{lin} stands for $\Gamma_{1a}(\mathbf{k})$ evaluated at the wave vector of the polaritons created in the OPA experiment (its **k** dependence within the one-photon line is assumed negligible). Note that we neglected $c_a(\mathbf{k},\omega)$ and $d_a(\mathbf{k},\omega)$, and in order to justify this, we will estimate the orders of magnitude of Γ_{2a}^{lin} and Γ_{3a}^{lin}. We do this by using Γ_{1a}^{lin} as obtained in the experiment, and the polariton transformation coefficients. From Ref. 4, it is found that a typical polariton in the OPA experiments has a group velocity $v_p \approx 2.10^5$ cm/s and differs in frequency by about 0.1 $\rm cm^{-1}$ from the **a** exciton. These data refer to the polariton in the branch closest to the exciton dispersion curve. In the dephasing rates Eqs. (5.11), however, summations over *both* polariton curves belonging to the relevant molecular transition are included. This is a natural consequence of the fact that the exciton at a given wave vector is a linear combination of upper and lower polaritons at that wave vector. Using Eqs. (4.11) and the oscillator strength of the **a** exciton as provided by Ref. 4, we find as estimates for the transformation coefficients of both branches the values given in Table I. For concreteness, we considered the case $\bar{\omega}_k < \bar{\Omega}_a$ (see Fig. 3), so that the upper polariton is closest to the **a**-exciton. The case $\bar{\omega}_k > \bar{\Omega}_a$ is obtained from this by simply interchanging the coefficients for the upper and lower branches and by adding some phase factors. In particular for y and z, no attempt was made to reach a high accuracy; the numbers present crude upper bounds to their absolute values. For the interaction matrix element, we used $\bar{V}_{ka} \approx -500\ {\rm cm}^{-1}$, as obtained from $\bar{\Omega}_a - \Omega_a$. From the values for x in the linear case, it is evident that only the term with $b = b' =$ upper in Eq. (5.11a) for Γ_{1a}^{lin} will contribute. Thus we have

$$\Gamma_{1a}^{lin} \approx \frac{\pi}{\hbar^2 N}\sum_{\mathbf{q}j}|F_{1a}(\mathbf{k},\mathbf{q})|^2\{\cdots\}, \tag{7.2}$$

where the factor in brackets has the same meaning as in Eq. (5.11a), except that only the upper polariton dispersion curve is used. Since in the frequency region of the OPA this dispersion curve is very close to the exciton dispersion curve, it is reasonable to view Γ_{1a}^{lin} as the exciton dephasing rate. Estimates for Γ_{2a}^{lin} and Γ_{3a}^{lin} follow by recognizing that in the absence of interbranch scattering (a good assumption, as the distance between upper and lower branch is of the order 10^3–$10^4\ {\rm cm}^{-1}$ at the relevant wave vector) again the only important contribution in Eqs. (5.11b) and (5.11c) are due to the term with $b = b' =$ upper. One then arrives at

$$\Gamma_{2a}^{lin} \approx \left(\frac{\bar{\omega}_k}{2\pi\hbar c^2\mu_{0a}^2}\right)^{1/2}\frac{x^*(w+y)}{2i}\Gamma_{1a}^{lin}, \tag{7.3a}$$

$$\Gamma_{3a}^{lin} \approx \left(\frac{\rho}{2\pi\hbar\bar{\omega}_k\mu_{0a}^2}\right)^{1/2}\frac{x^*(w-y)}{2i}\Gamma_{1a}^{lin}, \tag{7.3b}$$

where the coefficients should be taken from the upper polariton. For the OPA experiments, a typical value for Γ_{1a}^{lin} is 10 $\rm cm^{-1}$. Using, furthermore, the oscillator strength for the **a** exciton, we eventually find $c \approx 10^{-7}$ and $d \approx 10^{-3}$ as orders of magnitude for this specific experiment, so that these quantities may indeed be neglected.

TABLE I. The polariton transformation coefficients w, x, y, and z for upper and lower branches at two different wave vectors, which are characteristic for the linear and nonlinear optical experiments discussed in the text, respectively. The wave vectors are such that the upper (exciton-like) polariton has a group velocity of 2.10^5 cm/s in the linear case and 10^8 cm/s for the nonlinear case.

	Linear		Nonlinear	
	Upper	Lower	Upper	Lower
w	5.10^{-3}	1	0.26	0.98
x	i	$-4.10^{-3}i$	$0.97i$	$-0.21i$
y	5.10^{-4}	-10^{-3}	4.10^{-4}	-10^{-3}
z	$-8.10^{-3}i$	$-4.10^{-4}i$	$-8.10^{-3}i$	$2.10^{-3}i$

We next discuss the nonlinear experiments. In these, the laser is tuned close to half the frequency of the **a** exciton, so that our expression for $\chi^{(2)}$ may be written

$$\chi^{(2)}(-2\omega;\omega,\omega)=\chi_{\rm nr}^{(2)}+\frac{\rho}{2\hbar}\frac{\mu_{0a}\alpha_{a0}}{\bar{\Omega}_a-2\omega-i\Gamma_{1a}^{nl}}. \tag{7.4}$$

Here α_{a0} is a two-photon polarizability, containing a summation over all intermediate levels in the two-photon process, and Γ_{1a}^{nl} is $\Gamma_{1a}(\mathbf{k})$ evaluated at the wave vector relevant to the nonlinear experiment. Γ_{1a}^{nl} differs from Γ_{1a}^{lin}, because of the much higher group velocities of the polaritons ($v_p \approx 5.10^6$–10^8 cm/s) created in the phase-matched SHG and TPE experiments. For the extreme case of $v_p = 10^8$ cm/

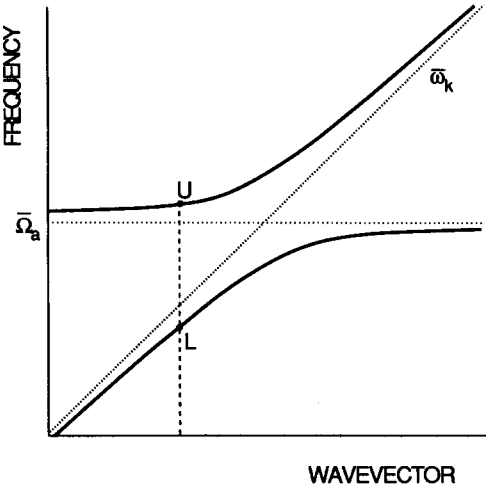

FIG. 3. Schematic representation of the polariton dispersion curves associated with the **a** exciton in naphthalene. The diagonal dotted line is the dispersion curve of photons with a background index of refraction ($\bar{\omega}_k = kc/\eta$); the horizontal line represents the **a** exciton at $\bar{\Omega}_a$, where an infinite effective mass has been assumed. At every wave vector, two polaritons with different frequencies are relevant (denoted U and L). In the calculation of the transformation coefficients in Sec. VII, a wave vector is assumed such that the upper polariton (U) is closest to the **a** exciton, as is the case in this figure.

s (corresponding to a polariton lying 6 cm^{-1} above the exciton curve), we give estimates for the transformation coefficients in Table I. It appears that even in this case, Γ_{1a}^{nl} must be almost completely due to the term with $b = b' =$ upper in Eq. (5.11a). Combining with Eq. (5.9), we then conclude that Γ_{1a}^{nl}, the width of the nonlinear profiles, may be viewed as the dephasing rate of the upper polariton. As mentioned earlier, the quantities $c_f(\mathbf{k},\omega)$ and $d_f(\mathbf{k},\omega)$, which enter the first order solution [cf. Eqs. (B8)], have been neglected in the second step of the iteration. In the nonlinear optical experiments under consideration, this is indeed justified because the laser frequency ω is not close to any material resonance, so that photon–exciton mixing for the signal at ω is negligible. It should be noted, that in the propagation of the nonlinear signal at $(2\mathbf{k},2\omega)$, the dielectric function $\epsilon(2\mathbf{k},2\omega) = 1 + 4\pi\chi^{(1)}(2\mathbf{k},2\omega)$ plays an important role. Consequently, also $c_a(2\mathbf{k},2\omega)$ and $d_a(2\mathbf{k},2\omega)$ affect the optical signal. Using similar approximations as in the linear case, we estimate these quantities to be 10^{-6} and -2.10^{-2}, respectively, which are still values small compared to 1. It is evident, however, that if the group velocity of the generated polaritons is increased further, the effect of d_a might become observable.

Although we did not derive an explicit expression for the third order susceptibility, it is clear that for the case of a two-photon resonance with the **a** exciton, we will obtain a resonant contribution with exactly the same frequency denominator as in Eq. (7.4). We conclude that our expressions for the susceptibilities agree with those used by Small and coworkers in the interpretation of their experiments, and, moreover, explain that different damping rates are observed in the linear and nonlinear optical experiments. At this point, we do not attempt to check the quantitative agreement between the observed widths and those predicted by us. Such a check would require detailed knowledge of the phonon dispersion curves in naphthalene and involve massive numerical integrations.

In this paper, the incorporation of damping by phonons has been based on the assumption that polaritons are the elementary excitations in the crystal. This, of course, is only true if the exciton-photon coupling is stronger than the exciton–phonon coupling, which is the case at low temperatures. A quantitative criterion is derived as follows. Consider an exciton and a photon with nearly degenerate frequencies (Ω), so that they are close to the intersection of the exciton and photon dispersion curve, where the polariton effects are strongest. The coupling between the exciton and photon is given by C as defined in Eq. (4.4a), and we have $C = f/2\eta$ [cf. Eq. (4.9)]. Let Γ_{ex} denote the damping rate of the bare exciton by phonons (Γ_{ex} may be obtained through OPA experiments). In the rotating wave approximation, the matrix to be diagonalized in order to find the collective eigenstates of the exciton–photon system is

$$\begin{pmatrix} \Omega & if/2\eta \\ -if/2\eta & \Omega - i\Gamma_{ex} \end{pmatrix}. \tag{7.5}$$

From this, it is easily shown that if $\Gamma_{ex} \gg f/\eta$, the amount of mixing of the photon and the exciton in the new eigenstates is only of the order $f/\eta\Gamma_{ex}$. Then, the polaritons, defined as the eigenstates of the matrix Eq. (7.5) without Γ_{ex}, are completely irrelevant, and Γ_{ex} will be the only damping rate appearing in susceptibilities, in the usual (phenomenological) way. If, however, $\Gamma_{ex} \ll f/\eta$, the new eigenstates as obtained from Eq. (7.5) are strongly mixed combinations of the photon and the exciton. Then, Γ_{ex} is an irrelevant quantity, and the only correct way to account for the effect of phonons is to view them as a perturbation to the polariton propagation as was done in this paper. The ratio $f/\eta\Gamma_{ex}$ as discriminator between strong and weak exciton–photon coupling, and thus as indicator of the importance of polariton effects, has been used by Small and co-workers already.[4,19] In naphthalene crystals below 20 K, $f/\eta\Gamma_{ex} \lesssim 0.2$, so that polariton effects may indeed be expected to be observable.

To conclude this paper, we discuss Ovander's formulation of nonlinear optical processes[18] mentioned in Sec. I. Starting from the model described in Sec. II, he first rewrites all material operators in the Hamiltonian Eq. (2.15) in terms of products of the Pauli operators $\hat{B}_{mf}$ and $\hat{B}_{mf}^{\dagger}$. This can, of course, be done in an exact way. The approximation is made, however, that these operators are Bose operators, so that $[\hat{B}_{mf}, \hat{B}_{ng}^{\dagger}] = \delta_{fg}\delta_{mn}$. We comment on this below. The Hamiltonian is now separated into a harmonic part, which is quadratic in the molecular and radiation creation and annihilation operators, and anharmonic terms, which are of higher order (third and fourth in the case of the electric dipole approximation). Using the Bose commutation relations, the quadratic part of the Hamiltonian is diagonalized through Tyablikov's procedure,[28] which yields the polaritons as approximate eigenmodes of the total (material and radiation) system. (If only H_{mat} is diagonalized in this way, the excitons are obtained.) Ovander proceeds by expressing the total Hamiltonian in terms of the, thus found, polariton creation and annihilation operators. The harmonic part then assumes, by definition, the simple form of a set of noninteracting harmonic oscillators (the bare polaritons). The anharmonic terms yield, even for the simplest approximations of the polariton transformation, a large number of interaction terms which are responsible for nonlinear processes,[18,19] and Ovander treats them as perturbations to the harmonic Hamiltonian. The Fermi golden rule is used to evaluate polariton fusion and fission rates, which are related to, e.g., the sum harmonic intensity, the Raman scattering intensity, etc., depending on the specific perturbation term under consideration.

Although, this procedure incorporates polaritons into nonlinear optics in an elegant way, it is rarely used in practice.[19] The reason is probably the complexity of the Hamiltonian after the polariton transformation has been carried out. For every different nonlinear optical process, a new rate has to be calculated. Susceptibilities of a given order, on the other hand, describe all processes of that order and are thus much more compact and convenient measures of the optical response. A second, more fundamental drawback of Ovander's scheme is that it relies completely on the Bose approximation for the Pauli operators. This is a linear approximation, which is usually argued to be valid for a low concentration of excited molecules. We note, however, that

this assumption is not consistent with the goal to describe nonlinear optical processes; extra nonlinearities must be expected when using the full commutators [Eq. (2.2)]. This becomes especially clear, if one considers two-level molecules. Using Bose commutators, implies that the population inversion operator vanishes identically, and consequently that the Heisenberg equations of motion for the molecular operators (the optical Bloch equations[3]) are linear. In other words, within the Bose approximation all nonlinear susceptibilities $\chi^{(2)}$, $\chi^{(3)}$, etc., vanish for a lattice of two-level systems. No attempt is made in Ovander's work to correct for this approximation. We note that, in principle, this can be done by using an exact transformation which expresses the original Pauli operators in terms of an infinite power series of new Bose operators.[9,28] This introduces an infinite number of extra anharmonic terms in the Hamiltonian (the "kinematic interaction"), and although the practical use of this transformation is cumbersome, this too, clearly shows the existence of extra nonlinearities. Finally, it should be noted that the Fermi golden rule does not suffice to treat nonlinear processes of order higher than 3; higher order perturbation theory has to be used to describe these.

ACKNOWLEDGMENT

The support of the National Science Foundation, The Office of Naval Research, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

APPENDIX A: EVALUATION OF THE KERNEL TERM

In this Appendix we derive Eq. (5.9) for the phonon damping of the polariton. In the lowest order of the perturbation expansion for the propagator $G(t,t')$ we have

$$\left(\frac{d\langle\hat{\xi}_{\mathbf{k}fb}(t)\rangle}{dt}\right)_{\rm ph} = -\int_{-\infty}^{t} dt' \langle\langle \hat{\xi}^{\dagger}_{\mathbf{k}fb} | L_{ep} e^{-iL_0(t-t')} Q L_{ep} | \sigma(t')\rangle\rangle . \tag{A1}$$

By construction, the reduced density operator $\hat{\sigma}(t')$ is diagonal in the phonon variables and since L_{ep} is linear in the phonon operators, the complementary projection $Q = 1 - P$ acts on $L_{ep}\hat{\sigma}(t')$ as the identity ($PL_{ep}\hat{\sigma}(t') = 0$) and may be omitted from Eq. (A1). Because of the hermitian character of L_{ep} and L_0 in Liouville space, we may now write

$$\langle\langle \hat{\xi}^{\dagger}_{\mathbf{k}fb} | L_{ep} e^{-iL_0(t-t')} L_{ep} | \hat{\sigma}(t')\rangle\rangle = \langle\langle L_{ep} e^{iL_0(t-t')} L_{ep} \hat{\xi}^{\dagger}_{\mathbf{k}fb} | \hat{\sigma}(t')\rangle\rangle . \tag{A2}$$

The total operator $L_{ep}\exp[iL_0(t-t')]L_{ep}\hat{\xi}^{\dagger}_{\mathbf{k}fb}$ contains direct products of polariton and phonon operators. The inner product of such a form with $\hat{\sigma}(t)$ is the exact expectation value of the hermitian conjugate of the polariton operator times the thermal equilibrium expectation value of the hermitian conjugate of the phonon operator. As explained in the main text, we use the approximation Eq. (5.8) for the interaction Hamiltonian $\hat{H}_{ep}$. Then it is readily shown that ($\tau \equiv t - t'$):

$$e^{iL_0\tau} L_{ep} \hat{\xi}^{\dagger}_{\mathbf{k}fb} = \frac{1}{\hbar\sqrt{N}} \sum_{\mathbf{q}j} F_{jf}(\mathbf{k},\mathbf{q}) \sum_{b'} x_{\mathbf{k}+\mathbf{q},fb'} x^{*}_{\mathbf{k}fb} e^{i\omega_{\mathbf{k}+\mathbf{q},fb'}\tau} \hat{\xi}^{\dagger}_{\mathbf{k}+\mathbf{q},fb'} \times (e^{-i\Omega_{\mathbf{q}j}\tau}\hat{b}_{\mathbf{q}j} + e^{i\Omega_{-\mathbf{q}j}\tau}\hat{b}^{\dagger}_{-\mathbf{q}j}) . \tag{A3}$$

Here, we used Bose commutation relations for the polaritons, since it is otherwise difficult to determine $\exp[iL_0\tau]$ analytically. We comment on this in Sec. V. From Eq. (A3) we get

$$L_{ep} e^{iL_0\tau} L_{ep} \hat{\xi}^{\dagger}_{\mathbf{k}fb} = \frac{1}{\hbar^2 N} \sum_{\substack{\mathbf{k}'\mathbf{q}'f' \\ \mathbf{q}j}} F_{ff'}(\mathbf{k}',\mathbf{q}') F_{jf}(\mathbf{k},\mathbf{q}) \times \sum_{b'b''b'''} x_{\mathbf{k}+\mathbf{q},fb'} x_{\mathbf{k}'+\mathbf{q}',fb''} x^{*}_{\mathbf{k}'fb'''} x^{*}_{\mathbf{k}fb} e^{i\omega_{\mathbf{k}+\mathbf{q},fb'}\tau} \times (\hat{C}_1 + \hat{C}_2) , \tag{A4}$$

with

$$\hat{C}_1 = [\hat{\xi}^{\dagger}_{\mathbf{k}'+\mathbf{q}',fb''} \hat{\xi}_{\mathbf{k}',fb'''}, \hat{\xi}^{\dagger}_{\mathbf{k}+\mathbf{q},fb'}] \times (\hat{b}_{\mathbf{q}'f'} + \hat{b}^{\dagger}_{-\mathbf{q}'f'})(e^{-i\Omega_{\mathbf{q}j}\tau}\hat{b}_{\mathbf{q}j} + e^{i\Omega_{-\mathbf{q}j}\tau}\hat{b}^{\dagger}_{-\mathbf{q}j}) \tag{A5a}$$

and

$$\hat{C}_2 = \hat{\xi}^{\dagger}_{\mathbf{k}+\mathbf{q},fb'} \hat{\xi}^{\dagger}_{\mathbf{k}'+\mathbf{q}',fb''} \hat{\xi}_{\mathbf{k}'fb'''} \times [\hat{b}_{\mathbf{q}'f'} + \hat{b}^{\dagger}_{-\mathbf{q}'f'}, e^{-i\Omega_{\mathbf{q}j}\tau}\hat{b}_{\mathbf{q}j} + e^{i\Omega_{-\mathbf{q}j}\tau}\hat{b}^{\dagger}_{-\mathbf{q}j}] . \tag{A5b}$$

After working out the commutator in Eq. (A5a), we get

$$\langle\langle \hat{C}_1 | \hat{\sigma}(t')\rangle\rangle = \mathrm{Tr}[\hat{C}_1^{\dagger}\hat{\sigma}(t')] = \langle\hat{\xi}_{\mathbf{k}fb''}(t')\rangle(\langle n_{\mathbf{q}j}\rangle_T e^{-i\Omega_{\mathbf{q}j}\tau} + \langle n_{-\mathbf{q}j}+1\rangle_T e^{i\Omega_{-\mathbf{q}j}\tau}) \times \delta_{\mathbf{k}',\mathbf{k}+\mathbf{q}}\delta_{\mathbf{q},-\mathbf{q}'}\delta_{j,f}\delta_{b',b'''} , \tag{A6}$$

with $\langle n_{\mathbf{q}j}\rangle_T$ the thermal occupation number of phonons with wave number $\mathbf{q}$ in branch j. Furthermore, the inner product of $\hat{C}_2$ with $\hat{\sigma}(t')$ is proportional to the expectation value of $\hat{\xi}^{\dagger}_{\mathbf{k}'fb''}\hat{\xi}_{\mathbf{k}'+\mathbf{q}',fb''}\hat{\xi}_{\mathbf{k}+\mathbf{q},fb'}$ at time t'. In a simplest treatment, in which we focus on the damping of a polariton neglecting the presence of other polaritons, this expectation value vanishes because of the action of two subsequent polariton annihilation operators on a state with at most one polariton. Clearly, this approximation is a linearization, which, however, is only involved in this relaxation term and not in the main equations of motion provided by the mean field term of Eq. (5.6). As the relaxation terms already present a perturbation to the main equations of motion, this approximation does not affect our results in a significant way. Combining Eqs. (A1)–(A6) we find

$$\left(\frac{d\langle\hat{\xi}_{\mathbf{k}fb}(t)\rangle}{dt}\right)_{ph} = -\int_{-\infty}^{t} dt' \frac{x_{\mathbf{k}fb}}{\hbar^2 N} \sum_{\mathbf{q}j} |F_{jf}(\mathbf{k},\mathbf{q})|^2 \times \sum_{b'b''} |x_{\mathbf{k}+\mathbf{q},fb'}|^2 x^{*}_{\mathbf{k}fb''} e^{-i\omega_{\mathbf{k}+\mathbf{q},fb'}(t-t')} \times (\langle n_{\mathbf{q}j}\rangle_T e^{i\Omega_{\mathbf{q}j}(t-t')} + \langle n_{-\mathbf{q}j}+1\rangle_T \times e^{-i\Omega_{-\mathbf{q}j}(t-t')})\langle\hat{\xi}_{\mathbf{k}fb''}(t')\rangle , \tag{A7}$$

which represents a relaxation equation with a time dependent relaxation rate. In the derivation of Eq. (A7) we used the relation $F_{jf}(\mathbf{k}+\mathbf{q},-\mathbf{q}) = F^*_{jf}(\mathbf{k},\mathbf{q})$ [cf. Ref. 8, p. 160]. We now perform the Markov approximation by going to the rotating frame for a moment,

$$\langle\hat{\xi}_{\mathbf{k}fb''}(t')\rangle \equiv \langle\hat{\Xi}_{\mathbf{k}fb''}(t')\rangle e^{-i\omega_{\mathbf{k}fb''}t'} \approx \langle\hat{\xi}_{\mathbf{k}fb''}(t)\rangle e^{-i\omega_{\mathbf{k}fb''}(t'-t)}, \tag{A8}$$

where the last step is justified because usually the damping (i.e., the time variation of $\langle\hat{\Xi}_{\mathbf{k}fb''}(t')\rangle$) is very slow compared to the polariton eigenfrequency $\omega_{\mathbf{k}fb''}$. The remaining integral over t' in Eq. (A7) is performed in the standard way,[13] namely, by adding a convergence factor $\exp[-\epsilon(t-t')]$ $(\epsilon\to 0^+)$, and in the final result we only keep the real part (a Dirac δ function in the involved frequencies), which corresponds to real relaxation processes. The imaginary part (a principal value integral) describes a frequency shift, which will be discarded here. We then arrive at Eq. (5.9).

APPENDIX B: ITERATIVE SOLUTION OF THE EQUATIONS OF MOTION

In this Appendix we show how the iteration of the equations of motion (5.12) is carried out and we explicitly derive expressions for the first and second order polarization. It proves useful to introduce the following new set of excitonic variables

$$\langle\hat{P}_{fg}(\mathbf{k},\omega)\rangle = \sqrt{N}\,(\langle\hat{B}_{\mathbf{k}fg}(\omega)\rangle + \langle\hat{B}_{\mathbf{k}gf}(\omega)\rangle) \quad (f\neq g) \tag{B1a}$$

$$\langle\hat{Q}_{fg}(\mathbf{k},\omega)\rangle = i\sqrt{N}\,(\langle\hat{B}_{\mathbf{k}fg}(\omega)\rangle - \langle\hat{B}_{\mathbf{k}gf}(\omega)\rangle) \quad (f\neq g) \tag{B1b}$$

$$\langle\hat{R}_f(\mathbf{k},\omega)\rangle = \sqrt{N}\,\langle\hat{B}_{\mathbf{k}ff}(\omega)\rangle. \tag{B1c}$$

Note that $\langle\hat{\mathbf{P}}_{fg}(\mathbf{k},\omega)\rangle = \langle\hat{\mathbf{P}}_{gf}(\mathbf{k},\omega)\rangle$ and $\langle\hat{\mathbf{Q}}_{fg}(\mathbf{k},\omega)\rangle = -\langle\hat{\mathbf{Q}}_{gf}(\mathbf{k},\omega)\rangle$. It is straightforward to rewrite the equations of motion in terms of these new variables. In doing so, the symmetries of the interaction matrix element $V_{\mathbf{k}}(gg';ff')$ with respect to interchange of its arguments (see Sec. II) may be exploited to reduce the complexity of the equations. We now assume for all variables discrete Fourier decompositions as in Eq. (6.1), with amplitudes $P_{fg}(\mathbf{k}_i,\omega_i)$, etc. In terms of these amplitudes, the equations of motion read

$$\begin{aligned}
-\omega_t P_{fg}(\mathbf{k}_t,\omega_t) = {} & -i\Omega_{fg}Q_{fg}(\mathbf{k}_t,\omega_t) - \frac{i}{\rho}\sum_{i,j}^{*}\sum_{f'<g'}\sum_{h\neq f,g} P_{f'g'}(\mathbf{k}_i,\omega_i)\,[V_{\mathbf{k}_i}(hf';fg')Q_{hg}(\mathbf{k}_j,\omega_j) \\
& + V_{\mathbf{k}_i}(hf';gg')Q_{hf}(\mathbf{k}_j,\omega_j)] - \frac{1}{\hbar}\sum_{i,j}^{*}\sum_{h\neq f,g}\frac{\mathbf{E}(\mathbf{k}_i,\omega_i)}{\omega_i}\cdot[\boldsymbol{\mu}_{hf}\Omega_{hf}P_{hg}(\mathbf{k}_j,\omega_j) + \boldsymbol{\mu}_{hg}\Omega_{hg}P_{hf}(\mathbf{k}_j,\omega_j)] \\
& - \frac{2\Omega_{fg}}{\hbar}\sum_{i,j}^{*}\frac{\boldsymbol{\mu}_{fg}\cdot\mathbf{E}(\mathbf{k}_i,\omega_i)}{\omega_i}\,[R_f(\mathbf{k}_j,\omega_j) - R_g(\mathbf{k}_j,\omega_j)] \\
& + \{\delta_{g0}(1-\delta_{f0})i[\Gamma_{1f}(\mathbf{k}_t)P_{f0}(\mathbf{k}_t,\omega_t) + 2\Gamma_{3f}(\mathbf{k}_t)\boldsymbol{\mu}_{0f}\cdot\mathbf{E}(\mathbf{k}_t,\omega_t)] + (f\leftrightarrow g)\},
\end{aligned} \tag{B2a}$$

$$\begin{aligned}
-\omega_t Q_{fg}(\mathbf{k}_t,\omega_t) = {} & i\Omega_{fg}P_{fg}(\mathbf{k}_t,\omega_t) + \frac{i}{\rho}\sum_{i,j}^{*}\sum_{f'<g'}\sum_{h\neq f,g} P_{f'g'}(\mathbf{k}_i,\omega_i)\,[V_{\mathbf{k}_i}(hf';fg')P_{hg}(\mathbf{k}_j,\omega_j) \\
& - V_{\mathbf{k}_i}(hf';gg')P_{hf}(\mathbf{k}_j,\omega_j)] + \frac{2i}{\rho}\sum_{i,j}^{*}\sum_{f'<g'}P_{f'g'}(\mathbf{k}_i,\omega_i)V_{\mathbf{k}_i}(ff';gg')\,[R_g(\mathbf{k}_j,\omega_j) - R_f(\mathbf{k}_j,\omega_j)] \\
& - \frac{1}{\hbar}\sum_{i,j}^{*}\sum_{h\neq f,g}\frac{\mathbf{E}(\mathbf{k}_i,\omega_i)}{\omega_i}\cdot[\boldsymbol{\mu}_{hf}\Omega_{hf}Q_{hg}(\mathbf{k}_j,\omega_j) - \boldsymbol{\mu}_{hg}\Omega_{hg}Q_{hf}(\mathbf{k}_j,\omega_j)] \\
& + \{\delta_{g0}(1-\delta_{f0})i\left[\Gamma_{1f}(\mathbf{k}_t)Q_{f0}(\mathbf{k}_t,\omega_t) - 2ic\Gamma_{2f}(\mathbf{k}_t)\boldsymbol{\mu}_{0f}\cdot\frac{\mathbf{E}(\mathbf{k}_t,\omega_t)}{\omega_t}\right] - (f\leftrightarrow g)\}
\end{aligned} \tag{B2b}$$

$$\begin{aligned}
-\omega_t R_f(\mathbf{k}_t,\omega_t) = {} & \frac{-i}{\rho}\sum_{i,j}^{*}\sum_{f'<g'}\sum_{h\neq f}P_{f'g'}(\mathbf{k}_i,\omega_i) \\
& \times V_{\mathbf{k}_i}(hf';fg')Q_{hf}(\mathbf{k}_j,\omega_j) \\
& - \frac{1}{\hbar}\sum_{i,j}^{*}\sum_{h\neq f}\frac{\mathbf{E}(\mathbf{k}_i,\omega_i)}{\omega_i}\cdot\boldsymbol{\mu}_{hf}\Omega_{hf}P_{hf}(\mathbf{k}_j,\omega_j).
\end{aligned} \tag{B2c}$$

In these equations, the asterisk on the summations over i and j denotes a restriction to terms with $\mathbf{k}_t = \mathbf{k}_i + \mathbf{k}_j$, $\omega_t = \omega_i + \omega_j$. Furthermore, we explicitly indicate the fact that the interaction matrix element $V(gg';ff')$ vanishes for $f=g$ or $f'=g'$ in the case of nonpolar molecules [cf. Eq. (2.6)].

Before carrying out specific steps in the iteration, it is instructive to outline the general scheme to exploit Eqs. (B2). For the Fourier amplitudes P, Q, and R we assume an expansion in the electric field amplitudes, as was done for the total polarization field in Eqs. (6.3) and (6.4). These expansions are substituted into Eqs. (B2) which may then be solved by equating terms of equal order in the electric field

amplitudes on the left- and right-hand sides. As an example, Eq. (B2c) reads in nth order

$$-\omega_t R_f^{(n)}(\mathbf{k}_t,\omega_t) = \frac{-i}{\rho}\sum_{m=0}^{n}\sum_{i,j}^{*}\sum_{f'<g'}\sum_{h\neq f} P_{f'g'}^{(m)}(\mathbf{k}_i,\omega_i) \times V_{\mathbf{k}_i}(hf';fg')Q_{hf}^{(n-m)}(\mathbf{k}_j,\omega_j) - \frac{1}{\hbar}\sum_{i,j}^{*}\sum_{h\neq f}\frac{\mathbf{E}(\mathbf{k}_i,\omega_i)\cdot\boldsymbol{\mu}_{hf}}{\omega_i}\Omega_{hf}P_{hf}^{(n-1)}(\mathbf{k}_j,\omega_j)\,. \tag{B3}$$

The $P^{(m)}$ for $m\neq n$ and $Q^{(n-m)}$ for $m\neq 0$ occurring on the right hand side of this equation are already known from the solution to the lower order iteration steps. Together with the analogous equations for $P^{(n)}$ and $Q^{(n)}$, Eq. (B3) constitutes a linear set of equations for the nth order variables, from which $P^{(n)}$ may be solved explicitly. This solution determines the nth order susceptibility, because the Fourier amplitude of the nth order polarization may be written

$$\mathbf{P}^{(n)}(\mathbf{k},\omega) = \sum_{f<g}\boldsymbol{\mu}_{fg}P_{fg}^{(n)}(\mathbf{k},\omega)\,, \tag{B4}$$

where we used Eqs. (2.3), (B1) and the fact that $\boldsymbol{\mu}_{fg}=\boldsymbol{\mu}_{gf}$ and $\boldsymbol{\mu}_{ff}=0$.

We now perform the first steps in the iteration. We assume that in the absence of electric fields the crystal is in thermodynamic equilibrium at low temperature, so that all molecules are in the ground state. From this, the zero'th order solution is readily obtained

$$P_{fg}^{(0)}(\mathbf{k},\omega) = Q_{fg}^{(0)}(\mathbf{k},\omega) = 0 \quad (\text{for all } f,g)$$
$$R_f^{(0)}(\mathbf{k},\omega) = \rho\delta_{\omega,0}\delta_{\mathbf{k},0}\delta_{f,0}\,, \tag{B5}$$

where Umklapp has been neglected in the form of $R_f^{(0)}$. Thus, $R_0(\mathbf{k},\omega)$ has a dc component $(\mathbf{k},\omega)=(0,0)$. Using this solution, the first order equations are found to be

$$-\omega_i P_{fg}^{(1)}(\mathbf{k}_i,\omega_i) = -i\Omega_{fg}Q_{fg}^{(1)}(\mathbf{k}_i,\omega_i) - \frac{2\rho}{\hbar}\Omega_{fg}\boldsymbol{\mu}_{fg}\cdot\frac{\mathbf{E}(\mathbf{k}_i,\omega_i)}{\omega_i}(\delta_{f0}-\delta_{g0}) + \{\delta_{g0}(1-\delta_{f0})i[\Gamma_{1f}(\mathbf{k}_i)P_{0f}^{(1)}(\mathbf{k}_i,\omega_i) + 2\Gamma_{3f}(\mathbf{k}_i)\boldsymbol{\mu}_{0f}\cdot\mathbf{E}(\mathbf{k}_i,\omega_i)] + (f\leftrightarrow g)\} \tag{B6a}$$

$$-\omega_i Q_{fg}^{(1)}(\mathbf{k}_i,\omega_i) = i\Omega_{fg}P_{fg}^{(1)}(\mathbf{k}_i,\omega_i) + 2i\sum_{f'<g'}P_{f'g'}^{(1)}(\mathbf{k}_i,\omega_i)V_{\mathbf{k}_i}(ff';gg')(\delta_{g0}-\delta_{f0}) - \{\delta_{g0}(1-\delta_{f0})i\left[\Gamma_{1f}(\mathbf{k}_i)Q_{0f}^{(1)}(\mathbf{k}_i,\omega_i) + \frac{2ic}{\omega_i}\Gamma_{2f}(\mathbf{k}_i)\boldsymbol{\mu}_{0f}\cdot\mathbf{E}(\mathbf{k}_i,\omega_i)\right] - (f\leftrightarrow g)\} \tag{B6b}$$

$$-\omega_i R_f^{(1)}(\mathbf{k}_i,\omega_i) = 0\,. \tag{B6c}$$

The last equation yields

$$R_f^{(1)}(\mathbf{k}_i,\omega_i) = 0 \quad (\text{for all } f)\,. \tag{B7a}$$

Furthermore, from the first two equations we easily obtain

$$P_{fg}^{(1)}(\mathbf{k}_i,\omega_i) = Q_{fg}^{(1)}(\mathbf{k}_i,\omega_i) = 0 \quad \text{if } f\neq 0 \text{ and } g\neq 0\,. \tag{B7b}$$

Therefore, the only nontrivial solutions in first order are $P_{fg}^{(1)}$ and $Q_{fg}^{(1)}$ with one of the coefficients f or g equal to zero. This is no surprise, because only these coherences can be reached from the ground state by one interaction with the radiation field. In view of the symmetries of P_{fg} and Q_{fg} with respect to interchange of f and g, it is sufficient to solve for the cases $f=0$, $g\neq 0$. From the set of equations for $P_{0g}^{(1)}$ and $Q_{0g}^{(1)}$, which now follows from Eqs. (B6a) and (B6b), $Q_{0g}^{(1)}$ is easily eliminated and a closed set of equations for the $P_{0g}^{(1)}$ ($g=1,\ldots,K$; K is the number of molecular excited states) is obtained. In general, the solution of this set requires the inversion of a $K\times K$ matrix. In order to obtain analytical results, however, we neglect interaction matrix elements which are not of the form $V_{\mathbf{k}}(gf;fg)$ or $V_{\mathbf{k}}(gg;ff)$ (at present, $f=0$), which decouples the equations for different g. The effect of the other transitions on $P_{0g}^{(1)}$ may be accounted for in a phenomenological way by rescaling the interaction by the background dielectric constant ($V\rightarrow\overline{V}\equiv V/\eta^2$), as was done in Sec. IV. It has already been mentioned in Sec. IV under what conditions mixing of the different molecular excited states may safely be neglected in dealing with the linear optics, and we will assume that these conditions apply. We then find

$$P_{0g}^{(1)}(\mathbf{k}_i,\omega_i) = \frac{2\rho\hbar^{-1}\Omega_g[1+c_g(\mathbf{k}_i,\omega_i)+id_g(\mathbf{k}_i,\omega_i)]}{-[\omega_i+i\Gamma_{1g}(\mathbf{k}_i)]^2+\Omega_g(\Omega_g+2\overline{V}_{\mathbf{k},g})} \times\boldsymbol{\mu}_{g0}\cdot\mathbf{E}(\mathbf{k}_i,\omega_i)\,, \tag{B8a}$$

$$Q_{0g}^{(1)}(\mathbf{k}_i,\omega_i) = \frac{i(\Omega_g+2\overline{V}_{\mathbf{k},g})}{\omega_i+i\Gamma_{1g}(\mathbf{k}_i)}P_{0g}^{(1)}(\mathbf{k}_i,\omega_i) + \frac{2c\Gamma_{2g}(\mathbf{k}_i)\boldsymbol{\mu}_{g0}\cdot\mathbf{E}(\mathbf{k}_i,\omega_i)}{\omega_i[\omega_i+i\Gamma_{1g}(\mathbf{k}_i)]}\,, \tag{B8b}$$

with

$$c_g(\mathbf{k},\omega) = -\frac{\hbar}{\rho\Omega_g}\Gamma_{1g}(\mathbf{k})\Gamma_{3g}(\mathbf{k})\,, \tag{B8c}$$

$$d_g(\mathbf{k},\omega) = \frac{\Gamma_{1g}(\mathbf{k})}{\omega}+\frac{\hbar\omega}{\rho\Omega_g}\Gamma_{3g}(\mathbf{k})+\frac{\hbar c}{\rho\omega}\Gamma_{2g}(\mathbf{k})\,. \tag{B8d}$$

Substituting Eqs. (B7b) and (B8a) into Eq. (B4) leads to Eq. (6.5) for the linear susceptibility.

We now move to the second order equations. We are interested in the Fourier amplitudes at $(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$, so that $(\mathbf{k}_i,\omega_i)$ and $(\mathbf{k}_j,\omega_j)$ in Eqs. (B2) can be chosen from (0,0) [the dc component of $R_0^{(0)}$], $(\mathbf{k}_1,\omega_1)$, $(\mathbf{k}_2,\omega_2)$ and $(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$. We then find

$$-(\omega_1+\omega_2)P^{(2)}_{fg}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2) = -i\Omega_{fg}Q^{(2)}_{fg}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$$
$$+\{\delta_{g0}(1-\delta_{f0})i\Gamma_{1f}(\mathbf{k}_1+\mathbf{k}_2)P^{(2)}_{0f}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)+(f\leftrightarrow g)\}+A_{fg}, \quad \text{(B9a)}$$

$$-(\omega_1+\omega_2)Q^{(2)}_{fg}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2) = i\Omega_{fg}P^{(2)}_{fg}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$$
$$+2i\sum_{f'<g'}V_{\mathbf{k}_1+\mathbf{k}_2}(ff';gg')(\delta_{g0}-\delta_{f0})P^{(2)}_{f'g'}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$$
$$-\{\delta_{g0}(1-\delta_{f0})i\Gamma_{1f}(\mathbf{k}_1+\mathbf{k}_2)Q^{(2)}_{0f}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)-(f\leftrightarrow g)\}+B_{fg}\,. \quad \text{(B9b)}$$

Here, the zeroth order solutions [Eq. (B5)] have been used explicitly, whereas the first order solutions [Eqs. (B7) and (B8)] are hidden in A_{fg} and B_{fg}, which are defined by

$$A_{fg} = -\frac{i}{\rho}\sum_{g'}\sum_{h\neq f,g}P^{(1)}_{0g'}(\mathbf{k}_1,\omega_1)\left[V_{\mathbf{k}_1}(h0;fg')Q^{(1)}_{hg}(\mathbf{k}_2,\omega_2)\right.$$
$$\left.+V_{\mathbf{k}_1}(h0;gg')Q^{(1)}_{hf}(\mathbf{k}_2,\omega_2)\right]$$
$$-\frac{1}{\hbar}\sum_{h\neq f,g}\frac{\mathbf{E}(\mathbf{k}_1,\omega_1)}{\omega_1}\cdot\left[\mu_{hf}\Omega_{hf}P^{(1)}_{hg}(\mathbf{k}_2,\omega_2)\right.$$
$$\left.+\mu_{hg}\Omega_{hg}P^{(1)}_{hf}(\mathbf{k}_2,\omega_2)\right]+(\mathbf{k}_1,\omega_1)\leftrightarrow(\mathbf{k}_2,\omega_2) \quad \text{(B10a)}$$

$$B_{fg} = \frac{i}{\rho}\sum_{g'}\sum_{h\neq f,g}P^{(1)}_{0g'}(\mathbf{k}_1,\omega_1)\left[V_{\mathbf{k}_1}(h0;fg')P^{(1)}_{hg}(\mathbf{k}_2,\omega_2)\right.$$
$$\left.-V_{\mathbf{k}_1}(h0;gg')P^{(1)}_{hf}(\mathbf{k}_2,\omega_2)\right]$$
$$-\frac{1}{\hbar}\sum_{h\neq f,g}\frac{\mathbf{E}(\mathbf{k}_1,\omega_1)}{\omega_1}\cdot\left[\mu_{hf}\Omega_{hf}Q^{(1)}_{hg}(\mathbf{k}_2,\omega_2)\right.$$
$$\left.-\mu_{hg}\Omega_{hg}Q^{(1)}_{hf}(\mathbf{k}_2,\omega_2)\right]+(\mathbf{k}_1,\omega_1)\leftrightarrow(\mathbf{k}_2,\omega_2)\,. \quad \text{(B10b)}$$

A_{fg} and B_{fg} are the (complicated) source terms for the equations for the second order variables $P^{(2)}_{fg}$ and $Q^{(2)}_{fg}$. The contributions due to interchange of $(\mathbf{k}_1,\omega_1)$ and $(\mathbf{k}_2,\omega_2)$ reflect the possibility for the system to interact with the different electric field components in arbitrary time order. Of course, these terms only exist if $(\mathbf{k}_1,\omega_1)\neq(\mathbf{k}_2,\omega_2)$. The equation for $R^{(2)}$ is not given, because it is not needed in order to solve for $P^{(2)}_{fg}$. As in the linear case, $Q^{(2)}_{fg}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$ is easily eliminated leaving a closed set of equations for $P^{(2)}_{fg}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2)$. Since it is sufficient to consider $f<g$, the solution in general involves the inversion of a $K(K-1)/2\times K(K-1)/2$ matrix. Using the same decoupling as in the linear case, a closed equation is obtained for every transition fg, and the formal solution in terms of A_{fg} and B_{fg} is then

$$P^{(2)}_{fg}(\mathbf{k}_1+\mathbf{k}_2,\omega_1+\omega_2) = \frac{i\Omega_{fg}B_{fg}+[(\omega_1+\omega_2)+i\Gamma_{1g}(\mathbf{k}_1+\mathbf{k}_2)\delta_{f0}]A_{fg}}{-[(\omega_1+\omega_2)+i\Gamma_{1g}(\mathbf{k}_1+\mathbf{k}_2)\delta_{f0}]^2+\Omega_{fg}(\Omega_{fg}-2V_{\mathbf{k}_1+\mathbf{k}_2,g}\delta_{f0})} \quad (\text{for } f<g)\,. \quad \text{(B11)}$$

Substituting the explicit forms of the first order solutions into A_{fg} and B_{fg}, and ignoring for simplicity $c(\mathbf{k},\omega)$ and $d(\mathbf{k},\omega)$ in Eq. (B8a) and Γ_{1g} and Γ_{2g} in Eq. (B8b) one arrives after careful book keeping at Eq. (6.7) for the second order susceptibility.

[1] N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).
[2] C. Flytzanis, in *Quantum Electronics V.I.*, edited by H. Rabin and C. L. Tang (Academic, New York, 1975), p. 1.
[3] Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
[4] S. H. Stevenson, M. A. Connolly, and G. J. Small, Chem. Phys. **128**, 157 (1988).
[5] T. S. Rose, R. Righini, and M. D. Fayer, Chem. Phys. Lett. **106**, 13 (1984); V. M. Agranovich, A. M. Ratner, and M. Salieva, Solid State Commun. **63**, 329 (1987); T. S. Rose, V. J. Newell, J. S. Meth, and M. D. Fayer, Chem. Phys. Lett. **145**, 475 (1988).
[6] P. N. Butcher, *Nonlinear Optical Phenomena* (Ohio University, Athens, Ohio, 1965).
[7] D. Bedeaux and N. Bloembergen, Physica **69**, 67 (1973).
[8] A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).
[9] V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter*, edited by V. M. Agranovich and A. A. Maradudin (North Holland, Amsterdam, 1982).
[10] J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963).
[11] J. L. Birman, in *Excitons*, edited by E. I. Rashba and M. D. Sturge (North Holland, Amsterdam, 1982).
[12] G. R. Meredith, J. Chem. Phys. **75**, 4317 (1981); **77**, 5863 (1982).
[13] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).
[14] (a) J. Knoester and S. Mukamel, Phys. Rev. A **39**, 1899 (1989); (b) J. J. Opt. Soc. Am. B **6**, 643 (1989).
[15] (a) M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford, London 1954); (b) U. Fano, Phys. Rev. **103**, 1202 (1956).
[16] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).
[17] V. M. Agranovich, Sov. Phys. JETP **37**, 307 (1960).
[18] L. N. Ovander, Sov. Phys. Usp. **8**, 337 (1965).
[19] G. J. Small, in *Excited States*, edited by E. C. Lim (Academic, New York, 1982).
[20] M. Orrit and P. Kottis, Adv. Chem. Phys. **74**, 1 (1988).
[21] J. J. Hopfield, Phys. Rev. **182**, 945 (1969).
[22] (a) Y. Masumoto, S. Shionoya, and T. Takagahara, Phys. Rev. Lett. **51**, 923 (1983); (b) T. Takagahara, Phys. Rev. B **31**, 8171 (1985).
[23] J. Aaviksoo, A. Freiberg, T. Reinot, and S. Savikhin, J. Lumin. **35**, 267 (1986).

[24]M. Dagenais and W. F. Sharfin, J. Opt. Soc. Am. B **2**, 1179 (1985); Phys. Rev. Lett. **58**, 1776 (1987).
[25]V. M. Agranovich and Yu V. Konobeev, Sov. Phys. Solid State **3**, 260 (1961).
[26]J. P. Hansen and I. R. MacDonald, *Theory of Simple Liquids* (Academic, New York, 1976).
[27]R. Zwanzig, Physica **30**, 1109 (1964); B. J. Berne, in *Modern Theoretical Chemistry 6* (Plenum, New York, 1977).
[28]S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum, New York, 1967).
[29]S. Mukamel, Phys. Rep. **93**, 1 (1982); Adv. Chem. Phys. **70**, 165 (1988).
[30]W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).
[31]A word of caution is in place concerning $\chi^{(2)}$ in naphthalene crystals, because the exciton transition is E_1–E_1 forbidden on symmetry grounds. The strong second order nonlinear optical signals are probably due to E_1–M_1 transitions, but, nevertheless, experiments are often fitted using results obtained in the electric dipole approximation. See, R. M. Hochstrasser and H. N. Sung, J. Chem. Phys. **66**, 3276 (1977).